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(54) Title: SUPPORTED POLYMERISATION CATALYST

(57) Abstract

The invention relates to supported ligands and catalysts for use in the polymerisation of olefinically unsaturated monomers such as vinylic monomers, comprising the use of a compound attached to support, the compound being capable of complexing with a transitional metal. Preferably the compound capable of complexing with a transition metal is a diimine such as a 1,4-diaza-1,3-butadiene, a 2-pyridinecarbaldehyde imine, an oxazolidone or a quinoline carbaldehyde. Preferably the catalysts are used in conjunction with an initiator comprising a homolytically clevable bond with a halogen atom. The application also discloses processes for attaching ligands to supports, and processes for using the catalysts disclosed in the application.

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SUPPORTED POLYMERISATION CATALYST

The present invention relates to immobilised supported polymerisation catalysts for atom transfer polymerisation of olefinically unsaturated monomers in which molecular weight control is achieved by the presence of certain transition metal, especially copper, complexes.

It is desirable to be able to produce high molecular weight polymers with a low molecular weight distribution by catalysed addition polymerisation, in particular of vinylic monomers. Hitherto this has been achieved by polymerising via ionic processes typically in the presence of organometallics such as alkyl lithium's which are sensitive as regards reaction with water and other protic species. As such monomers containing functional groups are not readily polymerised. The use of ionic systems also precludes the use of solvents which contain protic groups and/or impurities resulting in very stringent reaction conditions and reagent purity being employed.

More recently atom transfer polymerisation based on the combination of a transition metal halide and alkyl halide have been utilised. For example Matyjasewski (Macromolecules (1995), vol 28, pages 7901-7910 and WO96/30421) has described the use of CuX (where X=Cl, Br) in conjunction with bipyridine and an alkyl halide to give polymers of narrow molecular weight

distribution and controlled molecular weight. This system suffers from the disadvantage that the copper catalyst is partially soluble in the system and thus a mixture of homogeneous and heterogeneous polymerisation ensues. The level of catalyst which is active in solution is thus difficult to determine. The catalyst residues which are soluble in the reaction medium prove difficult to remove from the product. Percec (Macromolecules, (1995), vol. 28, page 1995) has extended Matyjasewski's work by utilising arenesulphonyl chlorides to replace alkyl chlorides, again this results in a mixture of homogeneous and heterogeneous polymerisation and catalyst residues are difficult to remove from the product. Sawamoto (Macromolecules, (1995), vol. 28, page 1721 and Macromolecules, (1997), vol. 30, page 2244) has also utilised a ruthenium based system for similar polymerisation of methacrylates. This system requires activation of monomer by an aluminium alkyl in order to achieve the best results, itself sensitive to reaction with protic species which is an inherent disadvantage. These systems have been described as proceeding via a free radical mechanism which suffers from the problem that the rate of termination is > 0 due to normal radical-radical combination and disproportionation reactions.

The inventors have found that the use of diimines such as 1,4-diaza-1,3-butadienes and 2-pyridinecarbaldehyde imines may be used in place of bipyridines. These ligands offer the advantage of homogeneous polymerisation and thus the level of active catalyst can be accurately controlled and only one polymerisation process ensues. This class of ligand also enables the control of the relative stability of the transition metal valencies, for example, Cu(I) and Cu(II), by altering ancillary

substituents and thus gives control over the nature of the products through control over the appropriate chemical equilibrium. Such a system is tolerant to trace impurities, trace levels of O_2 and functional monomers, and may even be conducted in aqueous media. This system is the subject of copending patent application number PCT/GB97/01587.

A further advantage of this system is that the presence of free-radical inhibitors traditionally used to inhibit polymerisation of commercial monomers in storage, such as 2, 6-di-tert-butyl-4-methylphenol (topanol), increases the rate of reaction of the invention. This means that lengthy purification of commercial monomers to remove such radical inhibitors is not required. Furthermore, this indicates that the system is not a free-radical process. This is contrary to Matajaszewski and Sawamoto who show free-radical based systems.

A difficulty identified by the inventors for the commercialisation of the radical polymerisation system of Matajazewski and Sawamoto, and the diimine-based system described above is that high levels of catalysts is required for acceptable rates of polymerisation. This means that catalyst is relatively expensive as it is not recycled/reused and it must be removed by lengthy procedures to prevent contamination of the final product and to keep production costs down.

The inventors have therefore identified a process for attaching the catalyst to supports which allows the catalyst to be easily recovered and produces products with substantially less contamination than previously described systems.

Such supported catalysts were expected by the inventors to clump together since each metal ion can coordinate with two-ligands, each of which is attached to a support. This would reduce the effectiveness of such supported systems. However, this has not been observed by the inventors. Furthermore, the metal ion is tightly bound to the ligands and does not leach off into the surrounding solution or product, allowing it to be reused.

A first aspect of the invention provides a supported ligand for use in catalysts for polymerisation of olefinically unsaturated monomers, especially vinylic monomers, said ligand being one or more compounds attached to a support.

Such a ligand has general formula:

$S(D)_n$ FORMULA 1

where: S is the support,

D is a compound attached to the support, said compound being capable of complexing with a transition metal.

n is an integer of one or more.

Preferably, the support is inorganic, such as silica, especially silica gel. Alternatively the support may be organic, especially an organic polymer, especially a cross-linked organic polymer, such as poly(styrene-w-divinylbenzone). Preferably the support is

in the form of beads. This latter form is particularly advantageous because it has a high surface area which allows the attachment of a large number of compounds, whilst presenting a large surface area to the medium to be catalysed.

The compound (D) may be adsorbed onto the support or covalently attached to the support.

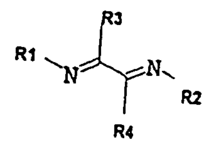
Preferably the compound is an organic compound comprising Schiff base, amine, hydroxyl, phosphine or diimine capable of complexing with a transition metal ion. Each Schiff base, amine, hydroxyl, phosphine or diimine is preferably separated from the support by a branched or straight alkyl chain, especially a chain containing 1 to 20 carbon atoms. The chain may comprise one or more aromatic groups as part of the alkyl chain.

One preferred ligand is the use of a support attached to two or more alkyl-amines, such as aminopropyl-, aminobutyl-, aminopentyl-, aminohexyl-, aminoheptyl- or aminooctyl- functionalised support. The amine groups are capable of forming a complex with one or more transition metal ions.

Especially preferred compounds are diimines.

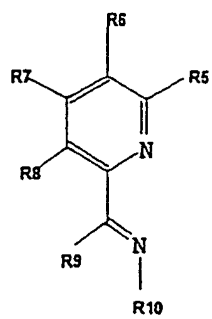
Preferably one of the nitrogens of the diimine is not part of an aromatic ring.

Preferably the diimine is a 1,4-diaza-1,3-butadiene



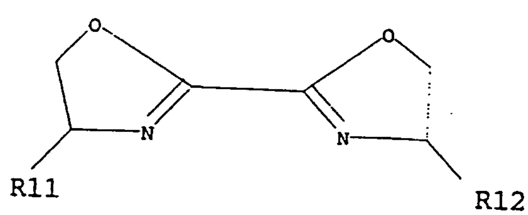
Formula 2

a 2-pyridinecarbaldehyde imine



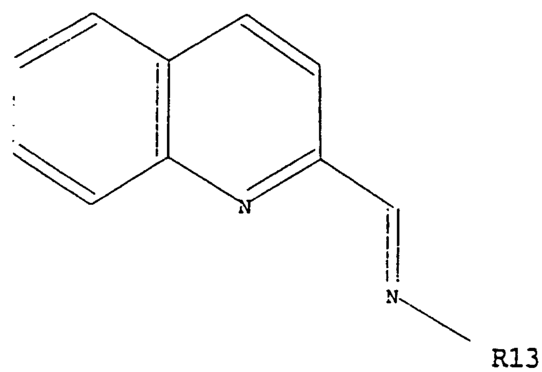
Formula 3

an Oxazolidone



Formula 4

or a Quinoline Carbaldehyde



Formula 5

where R_1, R_2, R_{10}, R_{11}, R_{12} and R_{13} may be varied independently and R_1, R_2, R_{10}, R_{11}, R_{12} and R_{13} may be H, straight chain, branched chain or cyclic saturated alkyl, hydroxyalkyl, carboxyalkyl, aryl (such as phenyl or phenyl substituted where
14 substitution is as described for R_4 to R_9), CH_2Ar (where Ar = aryl or substituted aryl) or a halogen. Preferably R_1, R_2, R_{10}, R_{11}, R_{12} and R_{13} may be a C_1 to C_{20} alkyl, hydroxyalkyl or carboxyalkyl, in particular C_1 to C_4 alkyl, especially methyl or ethyl, n-propylisopropyl, n-butyl, sec-butyl, tert-butyl, cyclohexyl, 2-ethylhexyl, octyl decyl or lauryl. R_1, R_2, R_{10}, R_{11}, R_{12} and R_{13} may especially be methyl.

R_3 to R_9 may independently be selected from the group described for R_1, R_2, R_{10}, R_{11}, R_{12} and R_{13} or additionally OC_nH_{2n+1} (where n is an integer from 1 to 20), NO_2, CN or O=CR (where R = alkyl, benzyl $PhCH_2$ or a substituted benzyl, preferably a C_1 to C_{20} alkyl, especially a C_1 to C_4 alkyl).

Furthermore, the compounds may exhibit a chiral centre α to one of the nitrogen groups. This allows the possibility for polymers having different stereochemistry structures to be produced.

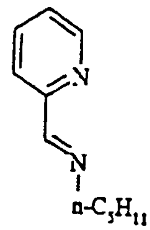
Compounds of general Formula 3 may comprise one or more fused rings on the pyridine group.

One or more adjacent R_1 and R_3, R_3 and R_4, R_4 and R_2, R_{10} and R_9, R_8 and R_9, R_8 and R_7, R_7 and R_6, R_6 and R_5 groups may be C_5 to C_8 cycloalkyl, cycloalkenyl, polycycloalkyl, polycycloalkenyl or cyclicaryl, such as cyclohexyl, cyclohexenyl or norborneyl.

The diimine compounds are preferably covalently attached to the support via positions R1, R2, R9, R10, R11, R12 or R13. They may be attached via a linkage group, such as a schiff base to the support.

Preferred diimines include:

Formula 6



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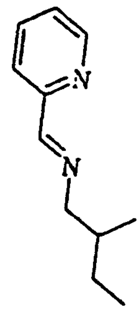

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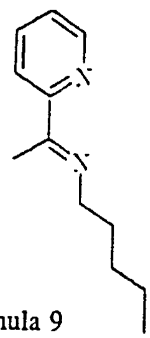

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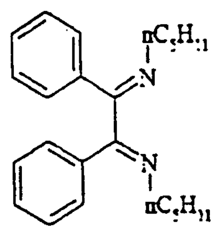

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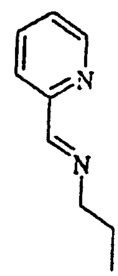

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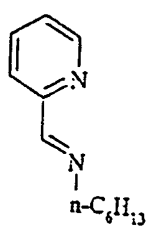

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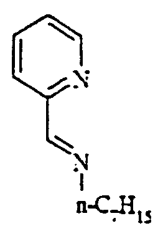

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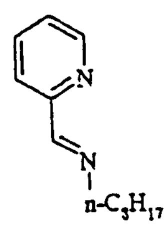

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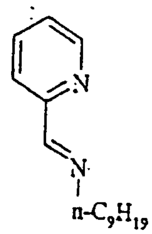

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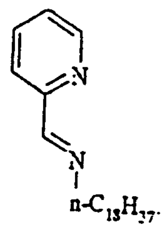

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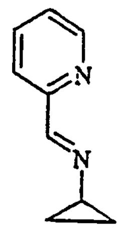

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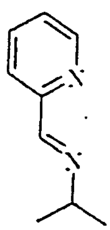

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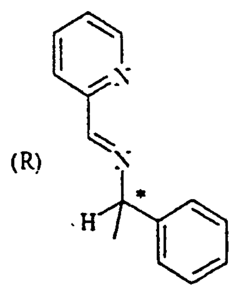

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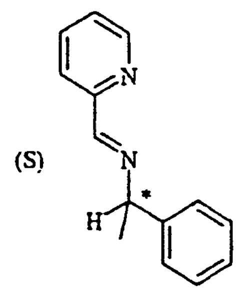

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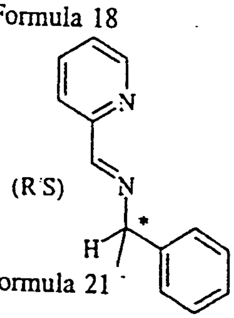

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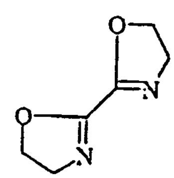

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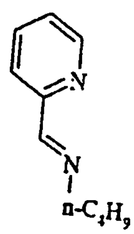

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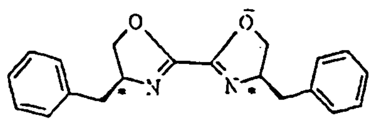
(S.S) 

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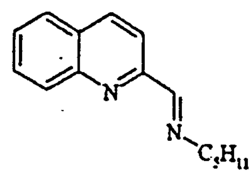

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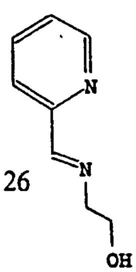

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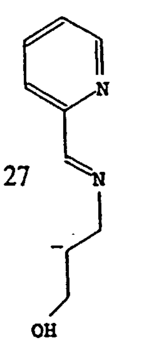

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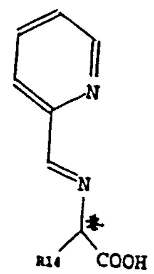
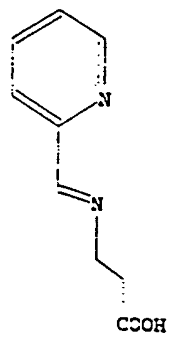


Formula 28

and



Formula 29

where: * indicates a chiral centre

R14 = Hydrogen, C_1 to C_{10} branched chain alkyl, carboxy- or hydroxy- C_1 to C_{10} alkyl.

The ligands, according to the first aspect of the invention may be used to form a catalyst for the addition polymerization of olefinically unsaturated monomers by using them in conjunction with:

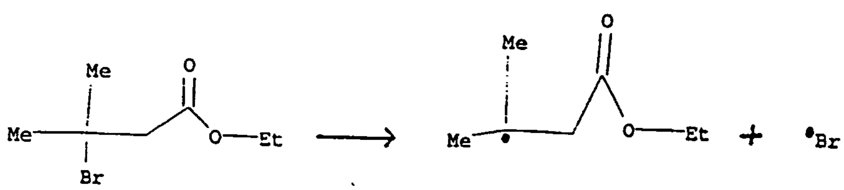
a) a compound of formula 30

MY

where M is a transition metal in a low valency state or a transition metal in a low valency state co-ordinated to at least one co-ordinating non-charged ligand and Y is a monovalent or polyvalent counterion; and

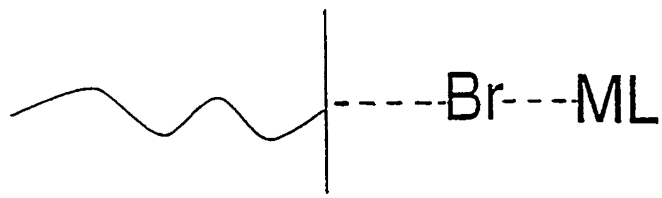
b) an initiator compound comprising a homolytically cleavable bond with a halogen atom.

Homolytically cleavable means a bond which breaks without integral charge formation on either atom by homolytic fission. Conventionally this produces a radical on the compound and a halogen atom radical. For example:



However, the increase in the rate of reaction observed by the inventors with free-radical inhibitors indicates that true free-radicals are not necessarily formed using the catalysts of the invention. It is believed that this possibly occurs in a concerted fashion whereby the monomer is inserted into the bond without formation of a discrete free radical species in the system. That is during propagation this results in the formation at a new carbon-carbon bond and a new

carbon-halogen bond without free-radical formation. The mechanism possibly involves bridging halogen atoms such as:



where:

ML is a transition metal-diimine complex.

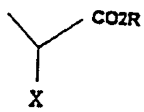
A "free-radical" is defined as an atom or group of atoms having an unpaired valence electron and which is a separate entity without other interactions.

Transition metals may have different valencies, for example Fe(II) and Fe(III), Cu(I) and Cu(II), a low valency state is the lower of the commonly occurring valencies, i.e. Fe(II) or Cu(I). Hence M in Formula 30 is preferably Cu(I), Fe(II), Co(II), Ru(II) or Ni(II), most preferably Cu(I). Preferably the co-ordinating ligand is $(CH_3CN)_4$.Y may be chosen from Cl, Br, F, I, NO_3, PF_6, BF_4, SO_4, CN, SPh, SCN, SePh or triflate (CF_3SO_3). Copper (I) triflate may be, which may be in the form of a commercially available benzene complex $(CF_3SO_3Cu)_2.C_6H_6$. The especially preferred compound used is CuBr.

Preferably the second component (b) is selected from:

RX

Formula 31



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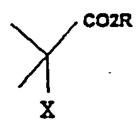

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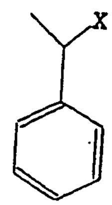

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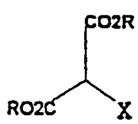

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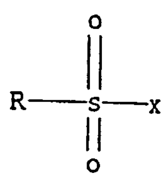

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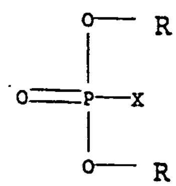

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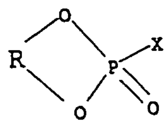
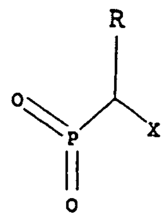
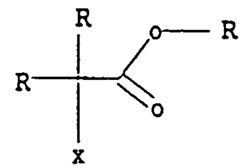


Formula 38

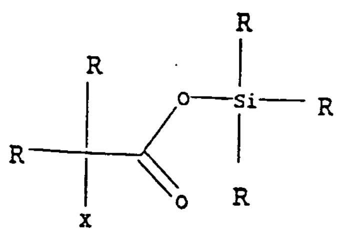


Formula 39



Formula 40

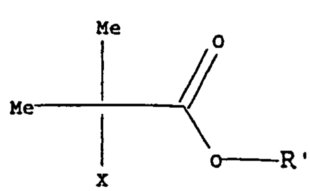
Formula 41



where R is independently selectable and is selected from straight, branched or cyclic alkyl, hydrogen, substituted alkyl, hydroxyalkyl, carboxyalkyl or substituted benzyl. Preferably the or each alkyl, hydroxyalkyl or carboxyalkyl contains 1 to 20, especially 1 to 5 carbon atoms.

X is a halide, especially I, Br, F or Cl.

The second component (b) may especially be selected from Formulae 43 to 52:



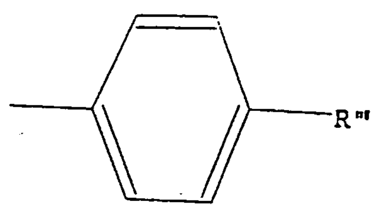
Formula 42

where:

X = Br, I or Cl, preferably Br

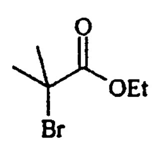
R' = -H,

$-(CH_2)_pR''$ (where m is a whole number, preferably p = 1 to 20, more preferably 1 to 10, most preferably 1 to 5, R" = H, oH, CooH, halide, NH_2, SO_3, CoX - where x is Br, I or C) or:

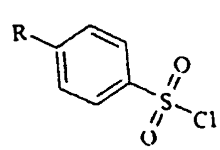


Formula 43

R^{III} = -COOH, -COX (where X is Br, I, F or Cl), -OH, $-NH_2$ or $-SO_3H$, especially 2-hydroxyethyl-2'-methyl-2' bromopropionate.

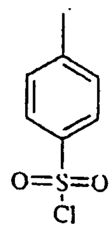


Formula 44

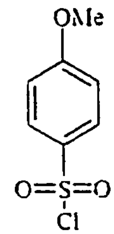


Formula 45

Especially preferred examples of Formula 45 are:

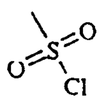


Formula 46A

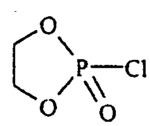


Formula 46B

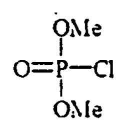
Br may be used instead at Cl in Formulae 46A and 46B.



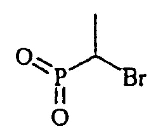
Formula 47



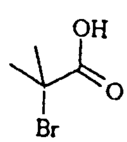
Formula 48F



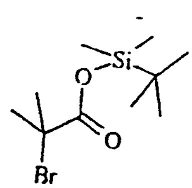
Formula 49



Formula 50

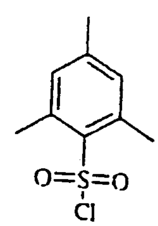


Formula 51



Formula 52 and

Formula 53



The careful selection of functional alkyl halides allows the production of terminally functionalised polymers. For example, the selection of a hydroxy containing alkyl

bromide allows the production of α-hydroxy terminal polymers. This can be achieved without the need of protecting group chemistry.

The transition metal may be precoordinated to the ligand covalently attached to its support.

Accordingly a second aspect of the invention provides a catalyst for use in the addition polymerisation of olefinically unsaturated monomers, especially vinyl monomers comprising a compound of general formula:

Formula 52 $[(SD)_cM]^{d+}A$

where: M = a transition metal in a low valency state or a transition metal co-ordinated to at least one co-ordinating non-charged ligand.

S = a support,

D = a compound attached to the support, the compound being capable of complexing with a transition metal,

d = an integer of 1 or 2,

c = an integer of 1 or 2,

A = a monovalent or divalent counter ion, such as Cl, Br, F, I, NO_3, PF_6, BF_4, SO_4, CN, SPh.

Preferably M is as defined for Formula 30 above. S may be as defined for Formula 1.

D may be adsorbed or covalently attached to the support.

D may be a compound as described earlier for the first aspect of the invention.

D may have one of the nitrogens as not part of a diimine ring.

D may be a diimine according to Formulae 2-29 as previously defined.

Preferably the catalyst is used with an initiator comprising a homolytically cleavable bond with a halogen atom, as previously defined. Preferred initiators are those defined in the first aspect of the invention according to Formulae 31 to 53.

A third aspect of the invention provides a process for the production of compound such as diimine covalently attached to supports, according to the first or second aspects of the invention.

The invention provides a process for producing a ligand for use in the catalysis of addition polymerisation of olefinically unsaturated monomers, especially vinylic monomers, comprising the steps of:

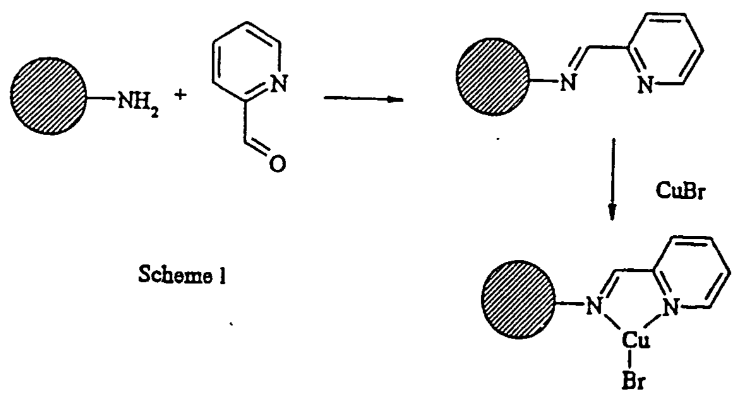
(a) providing a primary amine functionalised support;

(b) providing a ligand precusor comprising an aldehyde group or ketone group; and

(c) reacting the primary amine functionalised support with the ligand precursor to form a di i mine compound covalently attached to the support.

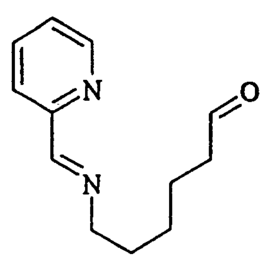
The primary amine of the functionalised support reacts with the aldehyde group or ketone group to form a Schiff base. Accordingly the diimine may be produced by

providing a ligand precursor with an aldehyde or ketone group replacing one of the imine groups of the final product, the reaction with the primary amine producing the second iimine group. This is shown in the reaction scheme below which shows the reaction of a support functionalised with a primary amine with 2-pyridine carbaldehyde to form a diimine attached to the support according to the first aspect of the invention. This can then be mixed with copper bromide or copper chloride to form a catalyst according to the second aspect of the invention.



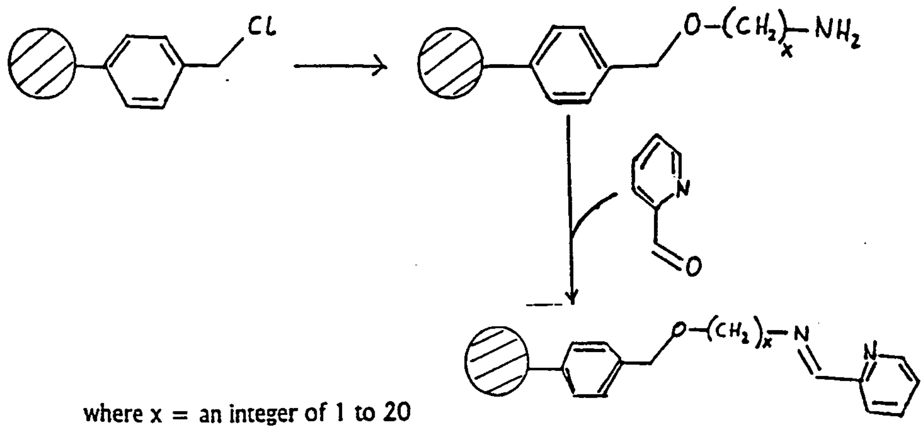
Scheme 1

Alternatively an aldehyde or a ketone group may be provided separately on a diimine ligand precusor. Such a suitable precursor is shown in Formula 53



This allows the diimine to be decoupled from the support to allow controlled polymerisation.

Alternatively the following reaction scheme may be followed:



where x = an integer of 1 to 20

The primary amine group may alternatively be provided on the ligand precursor and reacted with a ketone or aldehyde functionalised support.

The support material may be functionalised inorganic material, such as silica, especially silica gel. Alternatively functionalised organic support, especially a functionalised cross-linked polymeric support, such as poly(styrene-w-divinylbenzene) may be used. Such supports are preferably usually used for adsorbing compounds or in chromatography.

Preferably the reaction to form the Schiff base occurs at room temperature.

Preferably the functionalised support is an aminopropyl functional silica and the ligand precursor is 2-pyridine carbaldehyde.

The supported ligands and supported catalysts of the invention may be used in batch reactions or in continous reactions to polymerise olefinically unsaturated monomers. In the latter case, the supported catalyst or ligand may be packed into columns and the reaction mixture passed through.

The supported ligand or supported catalyst may be conveniently removed from a reaction mixture by for example filtration, precipitation or centrifugation. Alternatively the support may be magnetised beads and the catalyst is removed by means of a magnet.

The invention also provides the use of the catalyst according to the first or second aspect of the invention in the addition polymerisation of one or more olefinically unsaturated monomers and the polymerised products of such processes.

The components may be used together in any order.

The inventors have unexpectedly found that the catalyst will work at a wide variety of temperatures, including room temperature and as low as -15°C. Accordingly, preferably the catalyst is used at a temperature of -20°C to 200°C, especially -20°C to 150°C, 20°C to 130oC, more preferably 90°C.

The olefinically unsaturated monomer may be a methacrylic, an acrylate, a styrene, methacrylonitrile or a diene such as butadiene.

Examples of olefinically unsaturated monomers that may be polymerised include methyl methacrylate, vinylacetate, vinyl chloride acylonitonile, methacylamide, acrylamide, ethyl methacrylate, propyl methacrylate (all isomers), butyl methacrylate (all isomers), and other alkyl methacrylates; corresponding acrylates; also functionalised methacrylates and acrylates including glycidyl methacrylate, trimethoxysilyl propyl methacrylate, allyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, dialkylaminoalkyl methacrylates; fluoroalkyl (meth)acrylates; methacrylic acid, acrylic acid; fumaric acid (and esters), itaconic acid (and esters), maleic anhydride; styrene, α-methyl styrene; vinyl halides such as vinyl chloride and vinyl fluoride; acrylonitrile, methacrylonitrile; vinylidene halides of formula $CH_2 = C(Hal)_2$ where each halogen is independently Cl or F; optionally substituted butadienes of the formula $CH_2 = C(R^{15})\ C(R^{15}) = CH_2$ where R^{15} is independently H, C1 to C10 alkyl, Cl, or F; sulphonic acids or derivatives thereof of formula $CH_2 = CHSO_2OM$ wherein M is Na, K, Li, $N(R^{16})_4$ where each R^{16} is independently H or C_1 to C_{10} alkyl, D is COZ, ON, $N(R^{16})_2$ or SO_2OZ and Z is H, Li, Na, K or $N(R^{16})_4$; acrylamide or derivatives thereof of formula $CH_2 = CHCON(R^{16})_2$ and methacrylamide or derivative thereof of formula $CH_2 = C(CH_3)CON(R^{16})_2$. Mixtures of such monomers may be used.

Preferably, the monomers are commercially available and may comprise a free-radical inhibitor such as 2, 6-di-tert-butyl-4-methylpenol or methoxyplenol.

Preferably the co-catalysts are used in the ratios 0.01 to 1000 D : MY, preferably 0.1 to 10, and compound MY : initiator 0.0001 to 1000, preferably 0.1 to 10, where the degree of polymerisation is controlled by the ratio of monomer to (b) (expressed as molar ratios).

Preferably the components of the catalyst of the second aspect of the invention are added at a ratio M:initiator of 3:1 to 1:100.

Preferably the amount of diimine : metal used in the systems is between 1000:1 and 1:1, especially, 100:1 and 1:1, preferably 5:1 to 1:1, more preferably 3:1 to 1:1.

The ratio of RX:Copper is 1000:1 to 1:1, especially 100:1 to 1:1.

The reaction may take place with or without the presence of a solvent. Suitable solvents in which the catalyst, monomer and polymer product are sufficiently soluble for reactions to occur include water, protic and non-protic solvents including propionitrile, hexane, heptane, dimethoxyethane, diethoxyethane, tetrahydrofuran, ethylacetate, diethylether, N,N-dimethylformamide, anisole, acetonitrile, diphenylether, methylisobutyrate, butan-2-one, toluene and xylene. Especially preferred solvents are xylene and toluene, preferably the solvents are used at at least 1% by weight, more preferably at least 10% by weight.

Preferably the concentration of monomer in the solvents is 100% to 1%, preferably 100% to 5%.

The reaction may be undertaken under an inert atmosphere such as nitrogen or argon.

The reaction may be carried out in suspension, emulsion, mini-emulsion or in a dispersion.

Statistical copolymers may be produced using the catalysts according to the invention. Such copolymers may use 2 or more monomers in a range of ca.0-100% by weight of each of the monomers used.

Block copolymers may also be prepared by sequential addition of monomers to the reaction catalyst.

Telechelic polymers, may be produced using calalysts of the invention. For example, a functional initiator such as Formula 21 may be used with transformation of the w-Br group to a functional group such as -OH or -CO_2H via use of a suitable reactant such as sodium azide.

Comb and graft copolymers may be produced using the calalysts of the invention to allow, for example, polymers having functional side chains to be produced, by use of suitable reagents.

Embodiments of the invention will now be described by way of example and with reference to the following figure:

Figure 1 show the polymerisation of methylmethacrylate for four monomer additions to supported catalyst which has been collected at the end of each previous polymerisation reaction.

Figure 2 shows infrared spectra for the stepwise synthesis of pyridyl ligand onto cross-linked polystyrene beads.

Figure 3 shows kinetic reproducibility of silica supported atom transfer polymerisation from experiments carried out with diffeerent silica supported ligands synthesised at different times.

Figure 4 shows recycling experiments carried out with support S4 using the same conditions:

[MMA] : [Cu] : [Si-lig] : [E2 BI] = 100 : 1 : 3 : 1

Figure 5 shows reinitiation of PMMA.

Experimental

Reagents:

Methyl methacrylate (Aldrich, 99%) was purified by passing through a column of activated basic alumina to remove inhibitor. Copper(I) bromide (Aldrich, 98%) was purified according to the method of Keller & Wycoff. Toluene (Fisons, 99.8%) was dried over sodium. Ethyl-bromoisobutyrate (Aldrich, 98%), 2-pyridene carboxaldehyde, 3-aminipropyl-functionalised silica gel (Aldrich, 9% functionalised), silica gel (Merck), and iethyl ether (BDH, 98%) were used as received.

Ref: Keller, R.N.; Wycoff, H.D. Inorg. Synth. 2,1 (1946)

Characterisation:

Conversion was measured by gravimetry, and molecular weight distributions were measured using size exclusion chromatography (SEC) on a system equipped with a guard column, a mixed E column (Polymer Laboratories) and a refractive index detector, using tetrahydrofuran at 1 mL.min $^{-1}$ as an eluent. Poly(MMA) standards in the range (10^{6} - 200 g.mol $^{-1}$) were used to calibrate the SEC..

SiO_2, supported catalyst - covalently bound Schiff bases

Example 1:

2-pyridine carboxaldehyde (0.714 g, 6.67×10^{-3} mol) was added to 3-aminopropylfunctionalised silica gel (3.00 g, 3.15×10^{-3} mol of active NH_2) dispersed in diethyl ether (50 mL) and stirred for 1 hr. The diethyl ether was removed and the ligand functionalised silica gel washed with two aliquots of diethyl ether (50 mL), and dried under vacuum. The ligand functionalised silica gel was added to a Schlenk flask and purged with nitrogen. To this, a solution of toluene (30g), MMA (10g) and ethyl 2-bromoisobutyrate (0.138g) that was degassed by three freeze-pump-thaw cycles, was added. This was followed by the addition of copper(I) bromide (0.144g). The addition copper(I) bromide results in the SiO_2 supported catalyst. Agitation was effected by a magnetic stirrer. The mixture was then placed in an oil bath at 90oC to commence reaction. Samples were taken periodically for conversion and molecular weight analysis. After approximately 20 hr the mixture was cooled to room temperature and the SiO_2 supported catalyst allowed to settle. The polymer solution was removed via cannula, and the SiO_2 supported catalyst washed with two aliquots of toluene (50mL). To this, another solution of toluene, MMA and ethyl 2-bromoisobutyrate was added (concentrations as per previous solution) and the mixture placed in oil bath at 90oC. This procedure was repeated for two more monomer additions, demonstrating that the SiO_2 supported catalyst could be used at least four times for conssecutive reactions. The results are shown in table 1 and figure 1.

Poly(stryene-w-divinylbenzene) supported catalyst-covaltently bound Schiff base

Example 2:

2-pyridine carboxaldehyde (0.5 g, 6.67×10^{-3}) was added to aminofunctionalised cross-linked polystryene beads (1.30g) dispersed in tetrahydrofuran (50mL) and stirred for 1 hr. The tetrahydrofuran was removed and the ligand functionalised polystryene beads washed with two aliquots of tetrahydrofuran (50mL) and dried under vacuum. The ligand functionalised polystryene was added to a Schlenk flask and purges with nitrogen. To this, a solution of toluene (12g), MMA (4.0g) and ethyl 2-bromoisobutyrate (0.075g), that was degassed by three freeze-pump-thaw cycles, was added. This was followed by the addition of copper(I) bromide (0.057g). The addition copper(I) bromide produced the polystyrene supported catalyst. Agitation was effected by a magnetic stirrer. The mixture was then placed in an oil bath at 90oC to commence reaction. Samples were taken periodically for conversion and molecular weight analysis. After approximately 20 hr the mixture was cooled to room temperature and the polystyrene supported catalyst allowed to settle. The polymer solution was removed via cannula. The results are shown in table 1 and figure 2.

SiO_2 adsorbed catalyst

Example 3:

A solution of toluene (21g), MMA (7.1g), ethyl 2-bromoisobutyrate (0.139g) and N-^{n} octyl pyridylmethanimine (0.465g) that was degassed by three freeze-pump-thaw cycles, was added to Schlenk flask containing silica gel (3.0g).

To this, copper(I) bromide (0.095g) was added. Agitation was effected by a magnetic stirrer. The mixture was then placed in an oil bath at 90○C to commence reaction. Samples were taken periodically for conversion and molecular weight analysis. After approximately 20 hr the mixture was cooled to room temperature and the SiO_2 adsorbed catalyst allowed to settle. The polymer solution was removed via cannula. The results are shown in table 1.

SiO_2 adsorbed catalyst (II)- Non covalently bound on amino functionalised silica

Example 4:

A solution of toluene (21g), MMA (7.1g), ethyl 2-bromoisobutyrate (0.139g) and N-^{n}octyl pyridylmethanmine (0.465g) that was degassed by three freeze-pump-thaw cycles was added to Schlenk flask containing 3-aminopropyl-functionalised silica gel (3.0g). To this, copper(I) bromide (0.095g) was added. Agitation was effected by a magnetic stirrer. The mixture was then placed in an oil bath at 90○C to commence reaction. Samples were taken periodically for conversion and molecular weight analysis. After approximately 20 hr the mixture was cooled to room temperature and the SiO_2 adsorbed catalyst allowed to settle. The polymer solution was removed via cannula. The results are shown in table 1.

Table 1: Molecular weight and conversion results for examples 1 - 4.

Example	time /hr	Conversion	M_n	M_w	PDI
1A	1.33	0.458	21400	45800	2.14
1B	20	0.980	21000	45600	2.18
1C	26	-	-	-	-
1D	28	0.380	13600	40400	2.97
1E	30.5	0.726	18600	44600	2.39
1F	45	0.976	18700	46300	2.48
1G	49.25	-	-	-	-
1H	51.75	0.149	25000	46100	1.85
1I	70	0.942	24800	49600	2.00
1J	77.25	-	-	-	-
1K	77.83	0.031	21200	38500	1.81
1L	78.75	0.085	18300	37300	2.03
1M	92.5	0.760	11200	32200	2.37
2A	1	0.388	9030	17600	1.95
2B	2.33	0.681	11500	18900	1.64
2C	3.58	0.876	12800	21300	1.67
2D	17.92	0.986	13300	22600	1.70
3A	1	0.446	8950	15000	1.67
3B	2.33	0.666	10600	17000	1.61
3C	3.58	0.753	10200	15200	1.50
3D	17.92	0.817	10600	15800	1.50
4A	1	0.702	11400	20200	1.76
4B	2.33	0.891	5970	19700	3.31
4C	3.58	0.906	11800	21100	1.79
4D	17.92	0.922	11300	20800	1.84

	Time (min)	Conversion	Mn	Mw	PDi
5A	120	59	8600	15400	1.78
5B	300	83	9700	15600	1.61
5C	1380	96	11300	19200	1.70

Example 5:

$Ru(PPh_3)_3Cl_2$ on 3-aminopropyl-functionalised silica gel

0.14g $Ru(PPh_3)_3Cl_2$ (1.461×10^{-4} mol) together with 0.558 g (5.84×10^{-4} mol) 3-aminopropyl-functionalised silica gel (~ 9% functionalised; ~ 1.05 mmol NH_2/gram) was added to a schlenk and subjected to three vacuum-argon cycles. To this mixture was added 1.5 ml degassed MMA (1.395×10^{-2} mol) and 5 ml degassed xylene and the mixture heated to 96 °C and stirred. The polymerisation reaction was initiated by the addition of ethyl-2-bromoisobutyrate, 0.021 ml (1.430×10^{-4} mol), and the timer was started.

Samples were removed at regular intervals and the percentage conversion and molecular weight of the product polymer determined (conversions were by ^1H NMR)

Example 6:

$RuCl_3$ on 3-aminopropyl-functionalised silica gel

0.095 g $RuCl_3$ (4.65×10^{-4} mol) together with 1.86 g (1.395×10^{-3} mol) 3-aminopropyl-functionalised silica gel (~ 9% functionalised; ~ 1.05 mmol NH_2/gram) was added to a schlenk and subjected to three vacuum/argon cycles. To this mixture was added 5 ml degassed MMA (4.65×10^{-2} mol) and 15 ml degassed xylene and the mixture heated to 90°C and stirred. The polymerisation reaction was initiated by the addition of ethyl 2-bromoisobutyrate, 0.069 ml (4.65×10^{-4} mol), and the timer was started.

	Time (min)	Conversion %	Mn	Mw	PDi
6A	120	6.9	209000	336000	1.61
6B	300	15.1	192000	341000	1.775
6C	1380	74.2	84700	225000	2.65

Example 7:

$RhCl_3(H_2O)_3$ on 3-aminopropyl-functionalised silica gel

0.122 g $RhCl_3(H_2O)_3$ (4.65×10^{-4} mol) together with 1.86 g (1.395×10^{-3} mol) 3-aminpropyl-functionalised silica gel (~ 9% functionalised; ~ 1.05 mmol NH_2/gram) was added to a schlenk and subjected to three vacuum.argon cycles. To this mixture was added 5 ml degassed MMA (4.65×10^{-2} mol) and 15 ml degassed xylene and the mixture heated to 90oC and stirred. The polymerisation reaction was initiated by the addition of ethyl-2-bromoisobutyrate, 0.069 ml (4.65×10^{-4} mol), and the timer was started.

	Time (min)	Conversion	Mn	Mw	PDi
7A	120	6.1	93600	314000	3.35
7B	300	21.5	17900	320000	1.78
7C	1380	68.7	89100	243000	2.72

Example 8:

$Ag(CF_3CO_2)$ on 3-aminopropyl-functionalised silica gel

0.10g Ag(CF_3CO_2) (4.65×10^{-4} mol) together with 1.86g (1.395×10^{-3} mol) 3-aminopropyl-functionalised silica gel (~9% functionalised; ~1.05 mmol NH_2/gram) was added to a schlenk and subjected to three vacuum/argon cycles. To this mixture was added 5 ml degassed MMA (4.65×10^{-2} mol) and 15 ml degassed xylene and the mixture heated to 90oC and stirred. The polymerisation reaction was initiated by the addition of ethyl 2-bromoisobutyrate, 0.069 ml (4.65×10^{-4} mol) and the timer was started.

	Time (min)	Conversion	Mn	Mw	PDi
8A	120	2.6	61200	226000	3.68
8B	300	13.4	149000	324000	2.18
8C	1380	41.8	148000	299000	2.01

The precursor shown in Formula 53 may be produced by reacting 2-pyridine carbaldehyde with an α-aminocarboxylic acid, such as 8-amino caprylic acid, followed by mild reduction or byoupling of the parent acid through an amide link. It is envisaged that the use of amino acids will allow the incorporation of asymetry into the system.

SYNTHESIS OF POLYSTYRENE SUPPORT

The pyridyl route

Scheme The pyridyl route to ligand functionalised polystyrene support

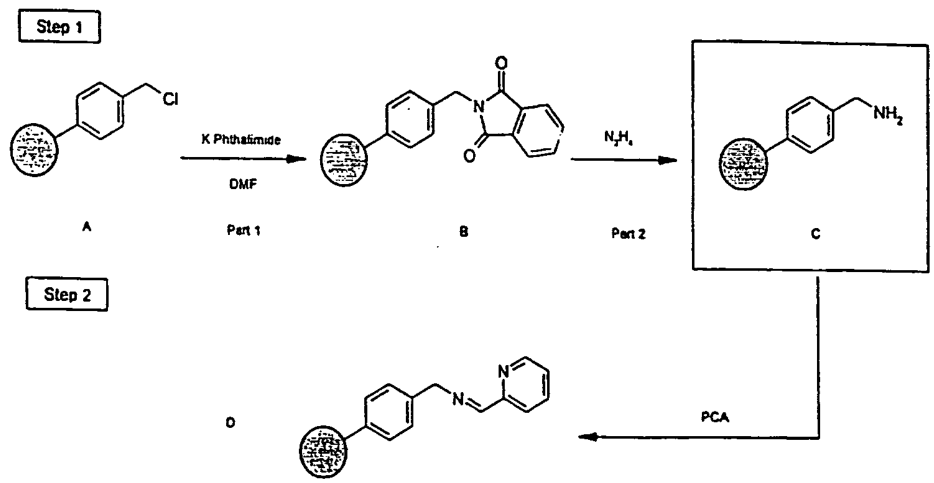


Table Comparison of synthesis techniques and characterisation of polystyrene supports synthesised via the pyridyl route.

n°	type	Step1 part1 *	Step1 part2 **	Step2 ***	n ligand/g by NMR (% vs th)	n Cu/g by ICP (% vs theory)	% retention between ICP and NMR
PS1	PS	1	1	1	1.75×10^{-3} (55.7)	1.38×10^{-3} (63.5)	98.5
PS2	PS	1	2	2	2.32×10^{-3} (71)	5.82×10^{-4} (26.8)	33.4
PS3	PS	2	2	2	3.09×10^{-3} (98.5)	?	?
PS4	PSm	2	3	2	1.27×10^{-3} (40.4)	?	?
PS5	PSp	2	2	2	2.84×10^{-3} (90.7)	?	?
PS6	PSp	2	2	2	$2.77 \times 10e^{-3}$ (88.6)	1.39×10^{-3} (80.6)	87.8
PS7	PSp	2	2	2	2.94×10^{-3} (94)	1.44×10^{-3} (66.9)	69.9

* Step1-part1 : 1=DMF, 50°C; 2=DMF, 110°C

** Step1-part2 : 1=DMF, RT; 2=EtOH, 80°C; 3=DMF, 90°C

*** Step2 : 1=Et2O, RT; 2=Toluene, 130°C, soxhlet; 3=Toluene, RT

Analysis of support

Table. **Infrared peak assignments for polystyrene supported ligands synthesised following the pyridyl route**

Support	type	functional groups	IR peak assignment (cm^{-1})
A	chloromethylated	CH2-Cl	1250
B	Phthalimido functions	C=O	1710, 1770
C	amino functions	NH2	1630, 3200
D	ligand functions	C=N	1490, 1600, 1650

Figure 2 shows infrared spectra for the stepwise synthesis of the pyridyl ligand onto cross-linked polystyrene beads.

Typical procedure for the synthesis of support PS5, PS6 and PS7

Step1-Part1 : Phthalimidomethylated cross-linked polystyrene beads (B)

To a stirred suspension of cross-linked chloromethylated beads (3 g, 12 mmol) in DMF (100 ml) was added potassium phthalimide (11.19g, 60.4 mmol) and the reaction mixture was heated at 110°C for 7h. After cooling, toluene (100 ml) was added and the reaction mixture was filtrated then washed with water (100 ml), methanol (100 ml) and diethyl ether (100 ml). The solid was dried under vacuum at RT for one day, then at 60°C overnight in a vacoven. Product : white solid (4.15 g).

IR absorption: 1710, 1770 cm-1 (ν C=O).

Elemental analysis: 80.64 %C, 5.85 %H, 3.49 %N (theoretical; 81.43 %C, 5.82 %H, 3.88 %N).

Step1-Part2 : Aminomethylated cross-linked polystyrene beads (C)

To a stirred suspension of phthalimide derivative (4.07g, 16.3 mmol) in ethanol (150 ml) was added hydrazine monohydrate (4.6 ml, 0.147 mol). The reaction mixture was heated at 80°C for 3h then cooled to room temperature and left overnight (careful, once the hydrazine has been added, you need enough solvent to compensate the swelling of the beads). Then the reaction mixture was filtered and the solid washed with water (100 ml), methanol (50 ml) and diethyl ether (50 ml). The solid was dried under vacuum at RT for one day, then at 60°C overnight in a vacoven. Product : white solid (3.24 g).

IR absorption: 1650, 1600, 1490 cm-1 (ν N-H?).

Elemental analysis: 76.61 %C, 6.56 %H, 8.48 %N (theoretical; 85.7 %C, 8.22 %H, 6.06 %N).

Step2 : Pyridiniminemethylated cross-linked polystyrene beads (D)

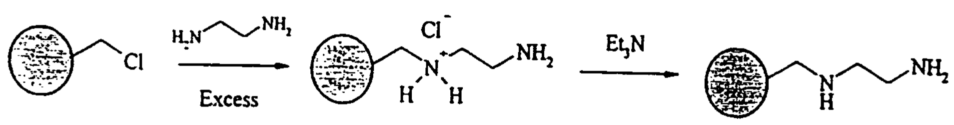
To a suspension of amino derivated support C (1.94 g, 7.74 mmol NH2) in toluene (50 ml) was added pyridine carbaldehyde (1.661 g, 15.3 mmol). The mixture was heated under reflux (130°C) in a soxhlet extractor in which the thimble contained 3A molecular sieves. The support was removed by filtration and washed successively with THF (50 ml), methanol (50 ml) and diethyl ether (50 ml) to give, after drying under reduced pressure at RT and 60°C overnight to constant weight, an orange solid (2.18 g).

IR absorption: 1650, 1600, 1490 cm-1 (ν C=N).

Elemental analysis: 81.06 %C, 6.5 %H, 8.05 %N (theoretical; 84.36 %C, 6.88 %H, 8.75 %N).

The (di)amine route

Scheme Example of cross-linked polystyrene beads functionalisation with ethylene diamine



Scheme. The different cross-linked polystyrene beads supported ligand obtained from the (di)amine route.

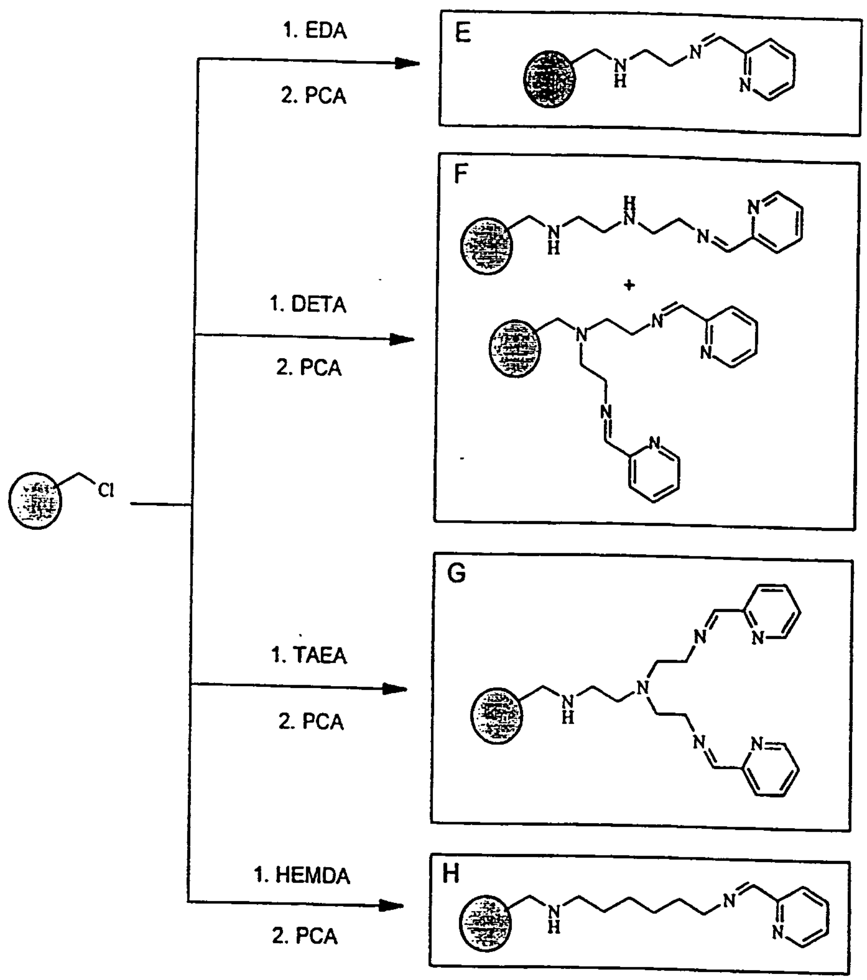


Table. Summary of cross-linked polystyrene supports synthesised following the (di)amine route.

Support	Support code	Amine used	Amine functionalisation reaction	**n ligand/g by NMR (% vs th)**
E	PS-EDA-lig	ethylene diamine	DA1	2.75 e^{-3} (99.7)
F	PS-DETA-lig	diethylene triamine	DA1	4.02 e^{-3} (99.5)
G	PS-TAEA-lig	tris(2-aminoethyl)amine	DA3	2.63 e^{-3} (70.8)
H	PS-HEMDA-lig	hexamethylenediamine	DA2	?

Procedure for synthesis of PS supports following the (di)amine route

Synthesis DA1 : (supports E & F)

A suspension of chloromethylated cross-linked polystyrene beads (3g, 4 mmol of Cl/g resin, 12 mmol) was shaken in round bottom flask with 15 ml amine during one day at room temperature. The polymer was filtered and successively rinsed two times with 10% triethylamine in dimethylformamide, once with DMF, four times with 10% Et3N in tetrahydrofuran, three times with THF and three times with methanol. The solid was then dried under vacuum at RT then at 80°C in the vacoven to constant weight.

Synthesis DA2 : (support H)

Same as DA1 but the amine is mix with 100 ml DMF in order to solubilised it.

Synthesis DA3 : (support G)

A suspension of chloromethylated cross-linked polystyrene beads (3g, 4 mmol of Cl/g resin, 12 mmol) in DMF (100 ml) was shaken in round bottom flask with tris(2-aminoethyl)amine (5 ml, 33.4 mmol) for 6h at 65°C under N2 atmosphere. After cooling to room temperature, the resin was filtered and washed successively

with two times with 10% triethylamine in dimethylformamide, once with DMF, four times with 10% Et3N in tetrahydrofuran, three times with THF and three times with methanol. The solid was then dried under vacuum at RT then at 80°C in the vacoven to constant weight.

The amino-hexanol route
of pyridine carbaldehyde, leading to the spaced supported ligand.

Scheme. Two different ways to the synthesis of hexanoxy supported ligand

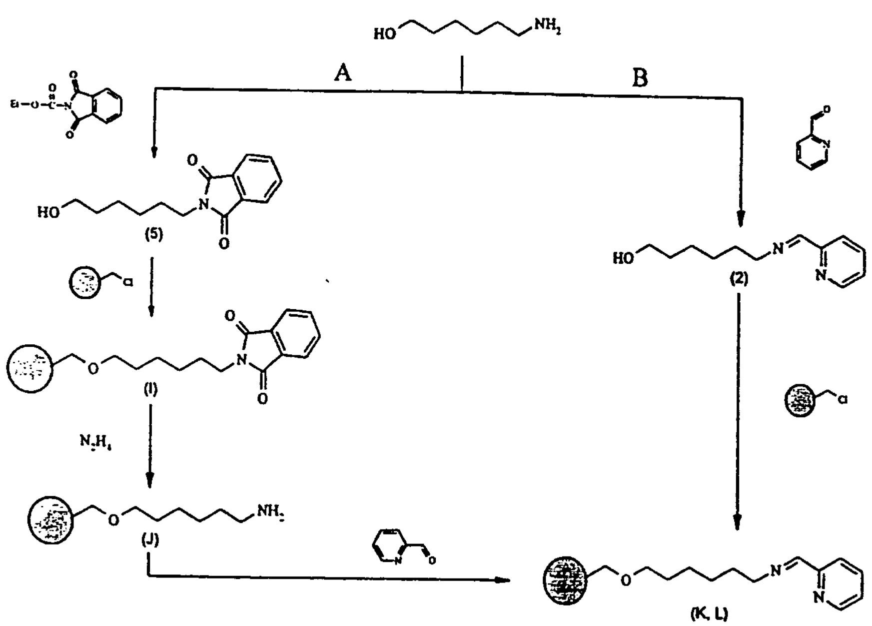


Table. Functionalisation of supports synthesised following the amino-hexanol route

Support	n ligand/g by NMR (% vs th)	n Cu/g by ICP (% vs theory)	% retention between ICP and NMR
K1	2.13×10^{-3} (90)	1.43×10^{-3} (80.5)	87.6
K2	2.16×10^{-3} (91)	1.12×10^{-3} (63.1)	68
L	?	9.25×10^{-4} (52.1)	?

Procedure for synthesis of polystyrene supports via the amino-hexanol route

N-^{n}hexanehydroxy-2-pyridine methanimine (2) :

6-phthalimido-1-hexanol (5) :

A solution of 6-amino-1-hexanol (7.54 g, 62.4 mmol) in 15 ml THF was added to a stirred slurry of N-(ethoxycarbonyl)phthalimide (14.08 g, 63 mmol) in 50 ml THF at 0°C (ice-water bath) with a pressure equalising funnel. After 5 minutes, the bath was removed and the mixture stirred overnight at ambient temperature. After removal of the solvent under reduce pressure, the compound was distillated (0.4 Torr) to give ethyl carbamate. The residue was put through a crystallisation procedure from a solution of toluene (25 ml) and hexane (10 ml) but the product stayed oily. The cristallisation started with scratching the product with spatula to give a light brown solid (13.9 g, 90 % yield).

^{1}H NMR: δ =7.81, 7.71 (m, 4H); 3.61 (m, 4H); 2.3 (s, 1H); 1.68, 1.39 (overlapping multiplets, 8H).

Elemental analysis: 67.8 %C, 6.9 %H, 5.7 %N (theoretical; 68 %C, 6.93 %H, 5.66 %N).

Route A : Phthalimidohexanoxy methylated cross-linked polystyrene beads (I) :
To a slurry of potassium hydride (0.81 g, 33.7 mmol) and tetrahydrofuran (100 ml) was added, with stirring, a solution of 6-phthalimido-1-hexanol *(5)* (5.92 g, 23.9 mmol), dibenzo-18-crown-6 (200 mg, 0.56 mmol) and hexamethylphosphoric triamide (10 ml). After 1 hour at ambient temperature, a slurry of chloromethylated polystyrene beads (3 g, 12 mequiv. Cl) in tetrahydrofuran (50 ml) was added. The reaction mixture was stirred and heated under reflux for 48 hours. The polymer was separated by filtration and washed successively with solutions of tetrahydrofuran/ethanol (1/1), tetrahydrofuran/methanol (1/1) and then with diethyl ether. The polymer was dried under redure pressure to constant weight to give a white solid (4.36 g, ~ 60 %).

IR absorption: 1710,1770 cm-1 (ν C=O),1075 cm-1 (ν C-O-C)

Route A : Aminohexanoxy methylated cross-linked polystyrene beads (J) :
Same procedure as for support C.

Route A : Pyridiniminehexanoxy methylated cross-linked polystyrene beads (K) :
Same procedure as for support D.

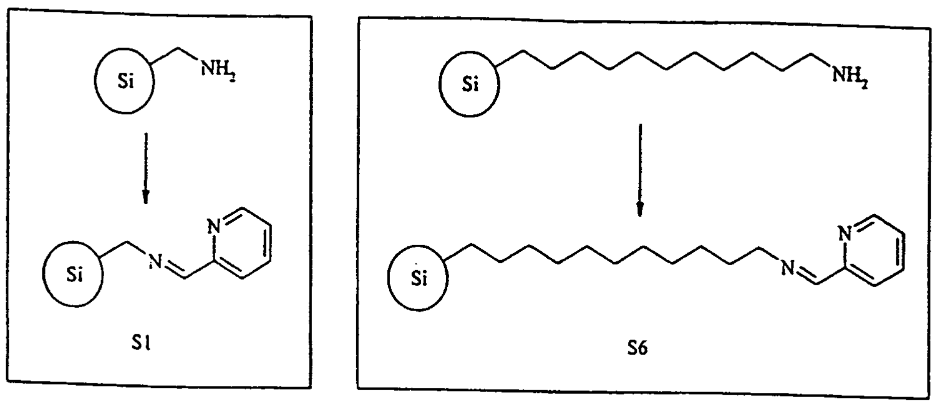
IR absorption: 1650 cm-1 (ν C=N).

Route B : Pyridiniminehexanoxy methylated cross-linked polystyrene beads (L) :
Same procedure as for support I, replacing phthalimido-hexanol (5) by N-ⁿhexanehydroxy-2-pyridine methanimine (2).

IR absorption: 1650 cm-1 (ν C=N).

Synthesis of silica support

Scheme. Two different silica supports synthesised by direct condensation of pyridine carbaldehyde onto the primary supported amine.



Supports S1 to S4 were found to be bright orange solids, although S5 was light yellow and S6 beige. Supports S1 to S5 were easily complexing copper bromide in methanol (black colour of the support). It took time to notice a change of colour for S6, when trying to complex CuBr.

Table Comparison of synthesis routes and characterisation of silica supported ligands.

Silica support	Step2 [a]	n ligand/g by NMR (% vs th)	n Cu/g by ICP (% vs theory)	% retention between ICP and NMR
S1	2[b]	$1.04\ e^{-3}$ (>100)	$7.08\ e^{-4}$ (84)	84
S2	2	$1.15\ e^{-3}$ (>100)	$7.92\ e^{-4}$ (93.8)	93.8
S3	2	$1.16e^{-3}$ (>100)	?	?
S4	2	$1.16\ e^{-3}$ (>100)	7.22×10^{-4} (85.6)	85.6
S5	3	$9.88\ e^{-4}$ (>100)	?	?
S6	1	?	?	?

[a] Step2 : 1=Et2O, RT; 2=Toluene, 130°C, soxhlet; 3=Toluene, RT
[b] Step2 method 2 : Typically mixture of 3-aminopropyl silica gel (15 g, 15.75 mmol) in toluene (150 ml) with pyridine carbaldehyde (3.6g, 33 mmol).

SILICA SUPPORTED ATOM TRANSFER POLYMERISATION

In a typical SSATP reaction, CuBr (0.134 g, 9.34×10^{-4} mol) and the support (x grams, depending on the experimentally calculated loading of ligand onto the support; [Si-lig]:[Cu] = n:1, where [Si-lig] is the concentration of ligand anchored to the silica support and n = 1, 2, 3, 4) were placed in a predried Schlenk flask which was evacuated and then flushed with nitrogen three times. Deoxygenated toluene (20 ml, 66% v/v) and deoxygenated methyl methacrylate (10 mL, 9.36×10^{-2} mol) were added and the suspension stirred. The flask was heated in a thermostatted oil bath at 90 °C and when the temperature had equilibrated ethyl-2-bromoisobutyrate (0.137 mL, 9.34×10^{-4} mol, [MMA]0:[In]0=100:1) was added. Samples (1-2 ml) were taken periodically after initiator was added. Conversions were calculated by gravimetry heating sample to constant weight overnight at 90°C under vacuum. The polymer was then diluted in THF and passed through basic aluminium oxide in order to remove the copper catalyst which has gone into solution.

Table Silica Supported Atom Transfer Polymerisations of MMA in toluene

Type[a]	Support[b]	[lig]/[Cu]	Time (min)	Conv. (%)	Mn*th*[d] (g/mol)	Mn(SEC) (g/mol)	PDI
ATP	/	2	60	15	1 500	3 430	1.14
			360	80	8 010	9 050	1.11
	SiNH2[c]	1	60	13	1 300	?	?
			300	34	3 400	182 800	2.1
	SiNH2	2	60	19	1 900	?	?
			300	52	5 200	146 300	1.94
SSATP	S1	1	60	27	2 700	19 700	1.63
			360	67	6 700	18 500	1.8
SSATP	S2	1	60	33	3 300	12 250	1.59
			360	75	7 510	15 950	1.56
SSATP	S2	2	60	48	4 800	12 200	1.6
			360	98	9 810	14 900	1.68
SSATP	S2bis	1	30	29	2 900	12 300	1.65
			300	76	7 610	18 200	1.64
SSATP	S3	2	30	35	3 500	12 800	1.68
			250	86	8 610	15 500	1.71
SSATP	S4	2	30	36	3 600	12 800	1.68
			260	91	9 110	16 350	1.78
SSATP	S5	2	30	30	3 000	18 900	2.1
			300	91	9 110	16 500	2.1
SSATP	S6	?	60	40	4 000	50 850	2.5
			240	74	7 410	50 800	2.4

[a] further data are available in annex

[c] 3-aminopropyl silica gel; here [lig] is equal to the concentration of amine functions on the silica support.

[d] Mn(th) = ([MMMA]0/[I]0 x MWMMA) x conversion, where MWMMA is the molecular weight of methyl methacrylate and [MMMA]0/[I]0 is the initial concentration ratio of MMA to initiator.

Figure 3 shows kinetic reproducibility of silica supported atom transfer polymerisation from experiments carried out with different silica supported ligands synthesised at different times.

Recycling experiments

Recycling experiments, using the same support, have also been carried out. Here, we present the results obtained when support S4 was used (some recycling experiments with support S2 are also available in § VI.3.2). A first polymerisation was carried out using 3 equivalents of silica supported ligand in reference to copper ([MMA]:[Cu]:[Si-lig S4]:[E2BI] = 100:1:3:1), then the solution medium was removed from the Schlenk tube with a syringe. The support, still carrying the transition metal catalyst, was washed three times with degassed toluene introduced and removed from the tube by syringe. The support was then dried under vacuum. During all this procedure, the support stayed in the schlenk tube and was kept under nitrogen in order to avoid any deactivation by contact with air. The washed support was then reused for a new polymerisation by introducing into the schlenk tube, in the following order : 20 ml of toluene, 10 ml of MMA and 0.137 ml of E2BI (same condition as before : [MMA]:[Cu]:[Si-lig]:[E2BI] = 100:1:3:1). Three recycling polymerisations were experimented with the same support.

Figure 4 shows recycling experiments carried out with support S4 using the same conditions; [MMA]:[Cu]:[Si-lig]:[E2BI] = 100:1:3:1

Each recycling experiment shows a decrease of the kinetic rate of polymerisation for MMA. However, recyclings 2 and 3 have the same kinetic behaviour. It seems that the catalyst activity is affected after each polymerisation. Probably, the amount of active species is reduce during the time of the experiment and the time of the washing of the support. This degradation finds a limit after a certain time or a certain number of recycling. The polydispersities still remain the same (around 1.7), even after several use of the support.

Table. Recycling experiments carried out with support S4 for the polymerisation of MMA by silica supported atom transfer polymerisation; [MMA]:[Cu]:[Si-lig]:[E2BI] = 100:1:3:1

Experiment[a]	Time (min)	Conversion (%)	Mnth (g/mol)	Mn(SEC) (g/mol)	PDI
First polym.	30	41	4 100	11 600	1.76
	180	90	9 010	13 800	1.8
Recycling 1	130	43	4 300	13 900	1.75
	330	81	8 110	16 850	1.69
Recycling 2	130	8	800		
	360	57	5 700	17 100	1.69
Recycling 3	130	8	800	?	?
	310	43	4 300	17 200	1.7

Influence of initiator and solvent on silica supported atom transfer polymerisation of MMA

Table. Influence of initiator and solvent on silica supported atom transfer polymerisation of MMA

Support	[lig]/[Cu]	Initiator[b]	Solvent	Conv.% (6h)	Mnth[c] (g/mol)	Mn(SEC) (g/mol)	PDI
S1	1	E2BI	Toluene	67	6 500	18 500	1.79
S1	1	DPB	Toluene	25	2 500	8 300	1.74
S1	1	TS	Toluene	38	3 800	9 200	1.74
S1	1	E2BI	Anisole	60	6 000	14 250	1.68
S1	1	E2BI	Phe2O	84	8 410	17 580	1.71

[b] E2BI : ethyl-2-bromoisobutyrate; DPB : 1,1,1-diphenyl methyl bromide; TS : tosyl bromide

[c] Mn(th) = ([MMMA]0/[I]0 x MWMMA) x conversion, where MWMMA is the molecular weight of methyl methacrylate and [MMMA]0/[I]0 is the initial concentration ratio of MMA to initiator.

RUTHENIUM SUPPORTED ATOM TRANSFER POLYMERISATION

Typical polymerisation procedure

In a typical reaction, for example [In]:[Ru]:[SiNH2] = 1:1:2, the ruthenium RuCl2(PPh3)3 (~0.45 g, 4.69 x 10^{-4} mol) and the support (~0.90 g, 9.49 x 10^{-4}) are introduced in a schlenk tube and subjected to three vacuum/nitrogen cycles. Deoxygenated toluene (15 ml, 75% v/v) and deoxygenated methyl methacrylate (5 ml, 4.67 x 10^{-2} mol) were added and the suspension stirred. The flask was heated in a thermostatted oil bath at 90 °C and when the temperature had equilibrated ethyl-2-bromoisobutyrate (0.069 mL, 4.69 x 10^{-4} mol, [MMA]0:[In]0=100:1) was added. Samples (1-2 ml) were taken approximately 15, 30, 60, 120, 180, 240 and 300 minutes after initiator was added. Conversions were calculated by gravimetry heating sample to constant weight overnight at 90 °C under vacuum. The polymer was then diluted in THF and passed through basic aluminium oxide in order to remove the ruthenium catalyst which has gone into solution.

Table. Molar ratios of components used in Silica supported-Ruthenium mediated-ATP

Experiment	[MMA]	[E2BI]	[RuCl2(PPh3)3]	[support][a]
1	100	2	1	4
2	100	1	1	4
3	100	0.5	1	4
4	100	1	2	8
5	100	1	0.5	2
6	100	1	1	8
7	100	1	1	2
8	100	1	0.5	silica[b]
9	100	1	0.5	Al2O3[c]
10[d]	100	2	1	4

[a] concentration of NH2 on 3-aminopropyl functionalised silica gel
[b] silica gel
[c] basic alumina
[d] reused the catalyst from experiment 1

Table. Results for silica supported-ruthenium mediated-ATP (SS-Ru-ATP)

Experiment	t (min)	Conversion (%)	Mnth (g/mol)	Mn (g/mol)	PDI
1	30	34	1 700	5 040	1.82
	180	90	4 550	6 780	1.56
2	30	40	4 000	6 750	1.76
	180	93	9 260	10 700	1.5
3	30	35	7 040	10 300	1.74
	240	91	18 200	21 500	1.49
4	30	46	4 600	6 530	1.56
	180	98	9 810	11 250	1.54
5	30	23	2 330	6 420	1.97
	180	78	7 770	10 500	1.55
6	30	39	3 900	8 000	3.1
	120	88	8 850	11 300	2.22
7	30	26	2 600	5 280	1.50
	180	75	7 510	8 380	1.47
8	45	18	1 800	5 780	1.51
	240	42	4 220	7 850	1.67
9	45	22	2 200	5 850	1.59
	180	40	4 000	7 240	1.57
10	30	25	1 250	4 930	2.14
	240	88	4 400	6 770	1.73

Reinitiation Experiments

In order to confirm the living character of this polymerisation, reinitiations from previously synthesised PMMA (made by silica supported-ruthenium mediated-ATP : SS-Ru-ATP) have been carried out. Two types of macroinitiators PMMA1 and PMMA2 have been synthesised following the conditions from experiments 4 and 7 respectively. They have been used for initiation of MMA and BzMA by SS-Ru-ATP, keeping the same catalyst and support quantities.

Table. **molar ratios of components used in silica supported-ruthenium mediated-ATP reinitiation experiments**

Experiment	Macroinitiator[a] ([In])	Monomer 2 ([M])	[RuCl2(PPh3)3]	[support][b]
11	PMMA1 (0.317)	MMA (100)	2	8
12	PMMA1 (0.317)	BzMA (63)	2	8
13	PMMA2 (0.338)	MMA (100)	1	2
14	PMMA2 (0.338)	BzMA (63)	1	2

[a] PMMA1 synthesised following conditions [E2BI]:[Ru]:[NH2] = 1:2:8, experiment 4
PMMA2 synthesised following conditions [E2BI]:[Ru]:[NH2] = 1:1:2, experiment 7
[b] concentration of NH2 on 3-aminopropyl functionalised silica gel

Table. Data for SS-Ru-ATP macroinitiation experiments using different monomers

Experiment	Mass targeted	Time (min)	Conv % 2nd pol°	Mnth (g/mol)	Mnexp (g/mol)	PDI
11	41600	0	0		10083	1.37
		30	30	20162	15230	1.57
		285	85	36736	31013	2.62
12	45040	0	0		10083	1.37
		30	60	30548	23262	1.60
		180	95	43297	37105	1.88
13	39080	0	0		9465	1.26
		30	30	18079	14282	1.37
		330	95	37147	29369	1.48
14	42280	0	0		9465	1.26
		30	55	27113	18132	1.35
		200	90	39535	26969	1.35

Polystyrene Supported Atom Transfer Polymerisation

Typical polymerisation procedure

In a typical PS-SATP reaction, CuBr (0.134 g, 9.34×10^{-4} mol) and the support (x grams. depending on the experimentally calculated loading of ligand onto the support; [PS-lig]:[Cu] = n:1, where [PS-lig] is the concentration of ligand anchored to the polystyrene support and n = 1, 2, 3, 4, etc...) were placed in a predried Schlenk flask which was evacuated and then flushed with nitrogen three times. Deoxygenated toluene (20 ml, 66% v/v) and deoxygenated methyl methacrylate (10 mL, 9.36×10^{-2} mol) were added and the suspension stirred. The flask was heated in a thermostatted oil bath at 90 °C and when the temperature had equilibrated ethyl-2-bromoisobutyrate (0.137 mL, 9.34×10^{-4} mol, [MMA]0:[In]0=100:1) was added. Samples (1-2 ml) were taken periodically after initiator was added. Conversions were calculated by gravimetry heating sample to constant weight overnight at 90°C under vacuum. The polymer was then diluted in THF and passed through basic aluminium oxide in order to remove the copper catalyst which has gone into solution.

Table. Polystyrene Supported Atom Transfer Polymerisations of MMA in toluene

Type	Support	[lig]/[Cu][b]	Time (min)	Conv. (%)	Mnth[c] (g/mol)	Mn(SEC) (g/mol)	PDI
ATP	/	2	60	15	1 500	3 430	1.14
			360	80	8 010	9 050	1.11
PS-SATP	PS2	1.25	33	29.6	2 960	14 020	1.55
			83	47.2	4 720	14 760	1.62
			120	55.6	5 560	16 510	1.51
			185	66.3	6 630	16 520	1.56
			245	72.2	7 230	15 500	1.66
			300	77.5	7 760	15 590	1.66
			363	83.6	8 370	16 230	1.62
PS-SATP	PS4	2	35	25.6	2 600	8 125	1.47
			310	84	8 400	11 150	1.63
PS-SATP	PS6	1.25	30	25.1	2 510	7 530	1.45
			61	36.7	3 670	8 670	1.54
			120	49.4	4 940	10 215	1.51
			180	60.1	6 010	11 140	1.53
			240	68.6	6 860	11 740	1.51
			300	75.2	7 530	11 670	1.56
PS-SATP	PS6 bis	1.25	32	25.1	2 510	6 950	1.41
			60	35.5	3 550	8 170	1.41
			147	55.1	5 510	9 880	1.41
			196	62.6	6 260	10 590	1.41
			240	67.5	6 750	10 710	1.43
			300	73.5	7 360	11 370	1.42
PS-SATP	PS7	1	31	20.9	2 100	8 320	1.42
			300	53.3	5 300	12 050	1.45
PS-SATP	PS7	2	31	28.5	2 800	7 580	1.39
			300	70	7 010	11 890	1.39

[b] Here [lig] is equal to the concentration of ligand functions on the polystyrene support.

[c] Mn(th) = ([MMMA]0/[I]0 x MWMMA) x conversion, where MWMMA is the molecular weight of methyl methacrylate and [MMMA]0/[I]0 is the initial concentration ratio of MMA to initiator.

Effect of the amount of polystyrene supported ligand

Table. Effect of the amount of polystyrene support on polystyrene supported atom transfer polymerisations of MMA in toluene

Support	[lig]/[Cu][b]	Time (min)	Conv. (%)	Mnth[c] (g/mol)	Mn(SEC) (g/mol)	PDI
PS7	1	31	20.9	2 090	8 320	1.42
		60	28.0	2 800	8 790	1.48
		123	38.5	3 850	10 510	1.44
		186	45.2	4 520	11 190	1.45
		253	50.4	5 040	12 550	1.39
		300	53.3	5 330	12 050	1.45
PS7	2	31	28.5	2 850	7 580	1.39
		60	35.7	3 570	8 110	1.43
		123	50.8	5 080	9 970	1.39
		186	59.8	5 980	11 130	1.36
		251	63.4	6 340	11 070	1.4
		300	70.0	7 010	11 890	1.39
PS7	3	31	34.9	3 490	7 870	1.43
		60	45.5	4 550	9 630	1.42
		123	60.9	6 090	11 390	1.44
		186	69.5	6 950	12 140	1.48
		252	78.9	7 900	12 940	1.48
		300	82.7	8 280	13 450	1.48
PS7	4	31	37.8	3 780	8 5900	1.55
		60	51.0	5 100	9 700	1.63
		123	69.7	6 970	11 120	1.68
		186	81.1	8 120	12 230	1.66
		252	87.2	8 730	13 510	1.59
		300	89.2	8 930	13 650	1.59

[b] Here [lig] is equal to the concentration of ligand functions on the polystyrene support.

[c] Mn(th) = ([MMMA]0/[I]0 x MWMMA) x conversion, where MWMMA is the molecular weight of methyl methacrylate and [MMMA]0/[I]0 is the initial concentration ratio of MMA to initiator.

The (di)amine route

Table. Experimental data for the PS-SATP of MMA mediated by copper catalyst complexed by different supports synthesised following the (di)amine route

Support	name	[Lig]0/[Cu]0	time (min)	Conv. (%)	Mn (th)[b]	Mn (SEC)	PDI (SEC)
E	PS-EDA-lig	~3	29	34.0	3 400	7 020	2.43
			241	96.0	9 610	13 900	2.09
G	PS-TAEA-lig	2.9	36	36.6	3 660	12 375	2.06
			312	95.2	9 530	15 890	1.95
H	PS-HEMDA-lig	2	30	25.8	2 580	16 050	1.78
			180	74.7	7 480	16 250	1.77
			292	93.5	9 360	16 150	1.8
F1	PS-DETA-lig	~5	36	44.1	4 410	10 440	2.61
			67	62.3	6 230	11 570	2.31
			131	83.1	8 320	12 950	2.15
			188	92.7	9 280	14 120	2.08
			250	99.1	9 920	17 110	1.79
F2	PS-DETA-lig	~5	29	38.6	3 860	9 200	2.02
			62	62.0	6 200	11 080	1.92
			126	82.2	8 230	13 250	1.86
			181	90.9	9 100	14 340	1.86
			241	96.6	9 670	14 640	1.89

[b] Mn(th) = ([MMMA]0/[I]0 x MWMMA) x conversion, where MWMMA is the molecular weight of methyl methacrylate and [MMMA]0/[I]0 is the initial concentration ratio of MMA to initiator.

The amino-hexanol route

Table. Experimental data for the PS-SATP of MMA mediated by copper catalyst complexed by different supports synthesised following the amino-hexanol route

Support	name	[Lig]0/[Cu]0	time (min)	Conv. (%)	Mn (th)[b]	Mn (SEC)	PDI (SEC)
PS7	PS-lig	2	31	28.5	2 850	7 580	1.39
			60	35.7	3 570	8 110	1.43
			123	50.8	5 080	9 970	1.39
			186	59.8	5 980	11 130	1.36
			251	63.4	6 340	11 070	1.4
			300	70.0	7 010	11 890	1.39
K1	PS-AHO-lig	2	30	27.1	2 710	13 880	1.81
			64	42.4	4 240	14 540	1.78
			119	58.9	5 890	15 670	1.75
			180	70.6	7 070	15 870	1.76
			244	79.8	7 990	18 040	1.6
			292	85.6	8 570	18 250	1.63
K2	PS-AHO-lig	2	30	26.8	2 680	10 370	1.6
			64	44.0	4 400	12 660	1.53
			119	61.0	6 100	14 730	1.53
			180	72.9	7 300	16 230	1.48
			244	82.5	8 260	16 660	1.51
			292	87.4	8 750	18 080	1.46
L	PS-AHO-lig	2	30	12.9	1 290	26 130	1.8
			64	19.1	1 910	26 950	1.81
			119	27.3	2 730	29 210	1.79
			180	33.9	3 390	29 390	1.83
			244	38.1	3 810	30 750	1.78
			292	42.9	4 290	29 920	1.84

[b] Mn(th) = ([MMMA]0/[I]0 x MWMMA) x conversion, where MWMMA is the molecular weight of methyl methacrylate and [MMMA]0/[I]0 is the initial concentration ratio of MMA to initiator.

REINITIATION EXPERIMENTS

In a typical reinitiation experiment, CuBr (0.134 g, 9.34 x 10^{-4} mol) and the macroinitiator (x grams, depending on the experimental molecular weight obtained from SEC and assuming that PDI = 1, [macroinitiator]:[Cu] = 0.182:1) were placed in a predried Schlenk flask which was evacuated and then flushed with nitrogen three times. Deoxygenated toluene (30 ml, 75% v/v) and deoxygenated methyl methacrylate (10 mL, 9.36 x 10^{-2} mol, [MMA]0:[Cu]0=100:1) or deoxygenated benzyl methacrylate (10 ml, 5.92 x 10^{-2} mol, [BzMA]0:[Cu]0=63.22:1) were added and the suspension stirred until all the macroinitiator is dissolved. The flask is then submitted to three Freeze-Pump-Thaw cycles (FPT). When the temperature had equilibrated to room temperature, N-^{n}pentyl-2-pyridine methanimine ligand (1) (0.36 ml, 1.87 x 10^{-3} mol, [Lig]0:[Cu]0=2:1) is added by syringe and the flask is heated straightforward in a thermostatted oil bath at 90 °C. Samples (1-2 ml) were taken periodically using syringes after the start of the heating. Conversions were calculated by gravimetry heating sample to constant weight overnight at 90°C under vacuum. The polymer was then diluted in THF and passed through basic aluminium oxide in order to remove the copper catalyst which has gone into solution.

Table. molar ratios of components used in reinitiation experiments***

Experiment	Macroinitiator[a]	[In]	Monomer 2 [MMA]	pentyl ligand [Lig]	[CuBr]
1	PMMA (A)	0.182	100	2	1
2	PMMA (S)	0.182	100	2	1
3	PMMA (P)	0.182	100	2	1
4	PMMA (L)	0.182	100	2	1

[a] PMMA (A) synthesised following conditions [MMA]:[CuBr]:[lig]:[E2BI] = 100:1:2:1

PMMA (S) synthesised following conditions [MMA]:[CuBr]:[Si-lig S4]:[E2BI] = 100:1:1:1

PMMA (P) synthesised following conditions [MMA]:[CuBr]:[PS-lig PS6]:[E2BI] = 100:1:1:1

PMMA (L) synthesised following conditions [MMA]:[CuBr]:[Si-lig S4]:[E2BI] = 100:1:2:1

These results are shown in Figure 5.

Table. Data for macroinitiation experiments using different monomers

Experiment	Macroinit.	Time (min)	Conv % 2nd pol°	Mnth (g/mol)	Mnexp (g/mol)	PDI
1	PMMA (A)	0	0		7 616	1.19
		34	10.5	13374	12 546	1.17
		63	15.1	15898	14 760	1.21
		130	22.1	19749	19 230	1.25
	61%~3h	186	26.9	22419	22 270	1.3
		244	30.6	24419	25 210	1.31
		278	32.5	25507	27 570	1.29
2	PMMA (S)	0	0		16 575	1.46
		33	10.4	22293	17 130	1.28
		62	15.1	24873	22 510	1.39
		129	22.2	28761	29 540	1.25
	2h	185	26.7	31244	31 330	1.27
		241	30.5	33366	34 640	1.25
		278	32.7	34534	35 810	1.25
3	PMMA (P)	0	0		13 105	1.25
		33	12.1	19773	18 770	1.17
		62	17.1	22493	20 510	1.19
		129	23.2	25853	23 940	1.20
		185	28.2	28608	26 300	1.20
		241	31.8	30617	28 440	1.21
		278	32.8	31143	29 150	1.22
4	PMMA (L)	0	0		6 896	1.46
		33	10.9	12862	12 250	1.19
		62	15.7	15508	14340	1.19
		129	23.3	19704	18 250	1.18
		185	27.3	21901	20 480	1.19
	69% 2h	241	30.8	23812	16 130	1.19
		278	33.3	25198	24 320	1.19

Block copolymerisation

Table. molar ratios of components used in reinitiation experiments

Experiment	Macroinitiator[a]	[In]	Monomer 2 [BzMA]	pentyl ligand [Lig]	[CuBr]
5	PMMA (A)	0.182	63.22	2	1
6	PMMA (S)	0.182	63.22	2	1
7	PMMA (P)	0.182	63.22	2	1
8	PMMA (L)	0.182	63.22	2	1

a PMMA (A) synthesised following conditions [MMA]:[CuBr]:[lig]:[E2BI] = 100:1:2:1

PMMA (S) synthesised following conditions [MMA]:[CuBr]:[Si-lig S4]:[E2BI] = 100:1:1:1

PMMA (P) synthesised following conditions [MMA]:[CuBr]:[PS-lig PS6]:[E2BI] = 100:1:1:1

PMMA (L) synthesised following conditions [MMA]:[CuBr]:[Si-lig S4]:[E2BI] = 100:1:2:1

Table. Data for macroinitiation experiments using different monomers

Experiment	Macroinit.	Time (min)	Conv % 2nd pol°	Mnth (g/mol)	Mnexp (g/mol)	PDI
5	PMMA (A)	0	0		7 616	1.19
		38	18.4	18890	17536	1.59
		64	23.0	21670	19861	1.28
		131	34.6	28790	26391	1.34
	61%~3h	261	73.0	52308	51028	1.83
		309	79.6	56348	45112	1.99
		358	80.2	56680	42 580	2.00
6	PMMA (S)	0	0		21 828	1.47
	s.2	33	19.9	33985	29395	1.75
		59	22.6	35647	30172	1.62
		126	35.4	43482	35658	1.58
	3h 62%	256	59.6	58283	45600	1.83
		304	71.1	65325	54698	1.80
		353	75.8	68207	55 380	1.79
7	PMMA (P)	0	0		14 676	1.23
		35	19.6	26689	24023	1.42
	3h	66	29.1	32497	28194	1.51
	52%	127	42.7	40790	35295	1.73
		257	63.3	53397	44560	1.71
		305	77.7	62208	53841	1.63
		354	83.8	65984	48 105	1.81
8	PMMA (L)	0	0		6 896	1.46
		36	16.7	17097		
		61	22.5	20673		
		128	37.0	29552		
		258	49.1	36922		
	69% 2h	306	52.2	38844		
		355	60.7	44070	28 240	1.83

Recyclability

Table. Recycling experiments carried out with support PS7 for the polymerisation of MMA by polystyrene supported atom transfer polymerisation; [MMA]:[Cu]:[PS-lig PS7]:[E2BI] = 100:1:2:1

Experiment	Time (min)	Conversion (%)	Mnth (g/mol)	Mn(SEC) (g/mol)	PDI
First polym.	31	28.5	2 850	7 580	1.39
	60	35.7	3 570	8 110	1.43
	123	50.8	5 080	9 970	1.39
	186	59.8	5 980	11 130	1.36
	251	63.4	6 340	11 070	1.4
	300	70.0	7 010	11 890	1.39
Recycling 1	29	4.06	400		
	69	7.04	700		
	134	15.4	1 540	12 000	1.68
	172	22.5	2 250	13 810	1.61
	255	38.1	3 810	14 760	1.65
	329	52.1	5 210	16 560	1.61
	365	58.5	5 850	16 880	1.59
Recycling 2	76	1.90	190		
	125	4.45	445		
	176	8.00	801		
	265	17.1	1714		
	336	25.7	2575		

CLAIMS

1. A supported ligand for use in catalysts for polymerisation of olefinically unsaturated monomers. especially vinylic monomers, said supported ligand having a general formula 1;

Formula 1 $S(D)_n$

where: S is the support,

D is a compound attached to the support, said compound being capable of complexing with a transition metal ion.

n is an integer of one or more.

2. A catalyst for use in the polymerisation of olefinically unsaturated monomers, comprising a compound of general formula:

Formula 52 $[(SD)_cM]^{d+}A$

where: M = a transition metal in a low valency state or a transition metal co-ordinated to at least one co-ordinating non-charged ligand.

S = a support,

D = a compound attached to the support, the compound being capable of complexing with a transition metal,

d = an integer of 1 or 2,

c = an integer of 1 or 2,

A = a monovalent or divalent counter ion.

3. A catalyst according to claim 2, wherein M is selected from Cu(I), Fe(II), Co(II), Ru(II) and Ni(II).

4. A supported ligand or a catalyst according to any preceding claim, wherein D is an organic compound comprising a group capable of complexing with a transition metal ion.

5. A supported ligand or a catalyst according to claim 4, wherein the group capable of complexing with a transition metal ion is selected from a Schiff base, amine, hydroxyl, phosphine or diimine.

6. A supported ligand or a catalyst according to claim 4 or claim 5, wherein the group capable of complexing with a transition metal ion is separated from the support by a substituted or non-substituted alkyl group.

7. A supported ligand or a catalyst according to claim 6, wherein the alkyl group is a straight chain, branched chain, or aromatic alkyl group.

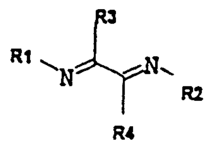
8. A supported ligand or a catalyst according to any preceding claim wherein compound D is a diimine.

9. A supported ligand or a catalyst according to claim 8, wherein one of the nitrogens of the diimine is not part of an aromatic ring.

10. A supported ligand or a catalyst according to claims 8 or 9, wherein the diimine is selected from:

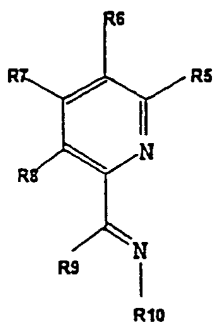
a 1.4-diaza- 1.3-butadiene

Formula 2



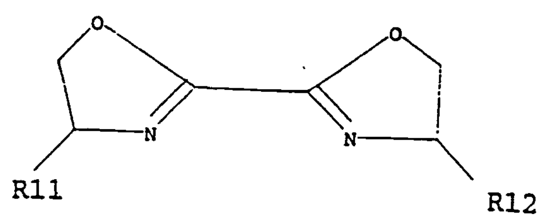
a 2-pyridinecarbaldehyde imine

Formula 3



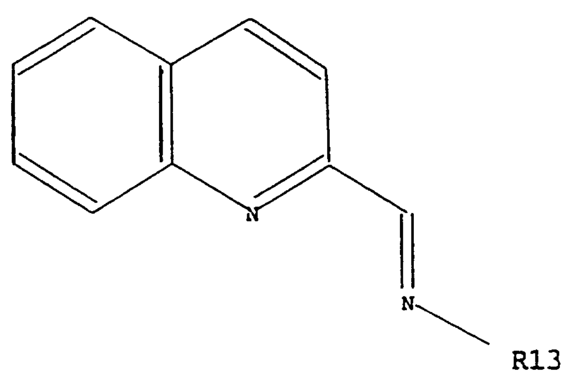
an Oxazolidone

Formula 4



or a Quinoline Carbaldehyde

Formula 5



where R_1, R_2, R_{10}, R_{11}, R_{12} and R_{13} may be varied independently and R_1, R_2, R_{10}, R_{11}, R_{12} and R_{13} may be H, straight chain, branched chain or cyclic saturated alkyl, hydroxyalkyl, carboxyalkyl, aryl (such as phenyl or substituted phenyl where substitution is as described for R_3 to R_9), CH_2Ar (where Ar = aryl or substituted aryl) or a halogen; and R_3 to R_9 may independently be selected from the group described for R_1, R_2, R_{10}, R_{11}, R_{12} and R_{13} or additionally OC_nH_{2n+1} (where n is an integer from 1 to 20), NO_2, CN or O = CR (where R = alkyl, benzyl $PhCH_2$ or a substituted benzyl).

11. A supported ligand or a catalyst according to any one of claims 5-10, wherein D exhibits a chiral centre α to one of the nitrogen groups.

12. A supported ligand or a catalyst according to claim 10 or claim 11, wherein D is a compound of general Formula 3 which comprises one or more fused rings on the pyridine group.

13. A supported ligand or a catalyst according to claim 10 or claim 11, wherein one or more adjacent R_1 and R_3, R_3 and R_4, R_4 and R_2, R_{10} and R_9, R_8 and R_9, R_8 and R_7, R_7 and R_6, R_6 and R_5 groups are selected from C_5 to C_8 cycloalkyl, cycloalkenyl, polycycloalkyl, polycycloalkenyl or cyclicaryl, such as cyclohexyl, cyclohexenyl or norborneyl.

14. A supported ligand or a catalyst according to any one of claims 8 to 13, wherein the diimine compound is covalently attached to the support via positions R1, R2, R9, R10, R11, R12 or R13.

15. A supported ligand or a catalyst according to any preceding claim, wherein D is attached to support S via a linkage group such as a Schiff base.

16. A supported ligand or a catalyst according to any preceding claim, wherein the support is selected from an inorganic compound such as silica, an organic polymer, and magnetised beads.

17. In combination, a supported ligand according to claim 1 complexed with a transition metal ion.

18. A combination according to claim 17, wherein the transition metal ion is in a low valency state.

19. A combination according to claim 18, wherein the transition metal is selected from Cu(I), Fe(II), Co(II), Ru(II) and Ni(II).

20. A catalyst for the addition polymerisation of olefinically unsaturated monomers comprising a supported ligand according to any one of claims 1 or 4-16 in combination with:

a) a compound of:

Formula 30 MY

where: M is a transition metal in a low valency state or a transition metal in a low valency state co-ordinated to at least one co-ordinating non-charged ligand.

Y is a mono- or polyvalent counter ion; and

b) an initiator compound comprising a homolytically cleavable bond with a halogen atom.

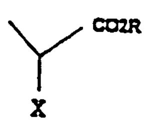
21. A catalyst according to claim 20, wherein the transition metal is selected from Cu(I), Fe(II), Co(II), Ru(II) and Ni(II).

22. A catalyst according to any one of claims 2 to 16 additionally comprising an initiator compound comprising a homolytically cleavable bond with a halogen atom.

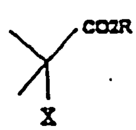
23. A catalyst according to any one of claims 2 to 16 or 20 to 22, wherein the co-ordinating ligand is $(CH_3CN)_4$.

24. A catalyst according to any one of claims 20-23, wherein the initiator compound is selected from:

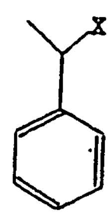
Formula 31 RX



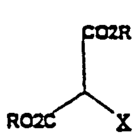
Formula 32



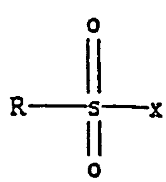
Formula 33



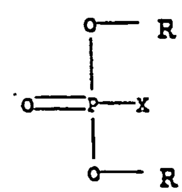
Formula 34



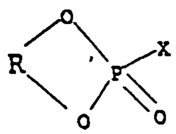
Formula 35



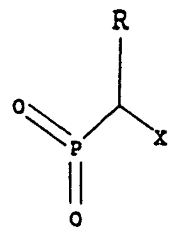
Formula 36



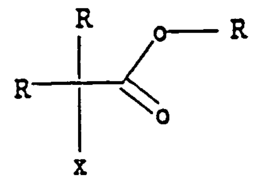
Formula 37



Formula 38

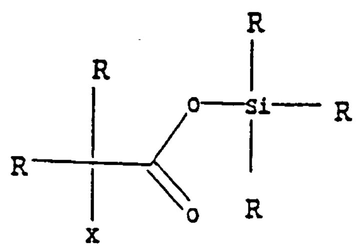


Formula 39



Formula 40

Formula 41



where: R is independently selectable and is selected from straight, branched or cyclic alkyl, hydrogen, substituted alkyl, hydroxyalkyl, carboxyalkyl or substituted benzyl.

X is a halide, especially I, Br, F or Cl.

25. A process for the production of a supported ligand, a catalyst or a combination according to any one of claims 8 to 24 comprising the steps of:

a) providing a functionalised support;

b) providing a ligand precursor, wherein one of the functionalised support or the ligand precursor comprises a primary amine, and the other of the functionalised support or the ligand precursor comprises an aldehyde or ketone group: and

c) reacting the primary amine with the aldehyde or ketone to form a diimine compound covalently attached to the support.

26. Process according to claim 25, wherein the diimine compound produced is then mixed with a transition metal halide to produce a diimine co-ordinated to a transition metal.

27. Process according to claim 26, wherein the transition metal halide is selected from CuCl and CuBr.

28. A process for the addition polymerisation of one or more olefinically unsaturated monomers comprising the use of a catalyst according to any one of claims 2 to 16 or 20 to 24.

29. A process according to claim 28, wherein the olefinically unsaturated monomer is selected from a methacrylic, an acrylate, a styrene, a methacrylonitrile or a diene.

30. A process according to claim 27 or claim 28, wherein the catalyst is used at a temperature between -20°C and 200°C.

31. A process according to any one of claims 28 to 30, additionally comprising the use of a free-radical inhibitor.

32. A process according to any one of claims 28 to 30, wherein the amount of D : MY is between 0.01 to 1000 and ratio of MY : initiator is 0.0001 to 1000.

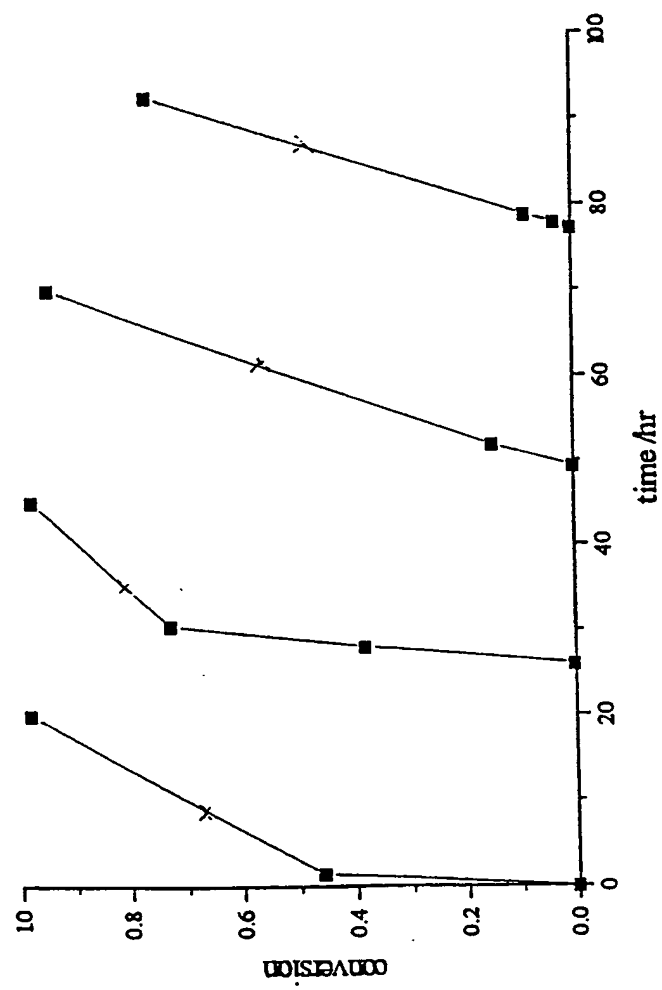


Figure 1: Conversion vs time for the four monomer additions in example 1.

FIGURE 2

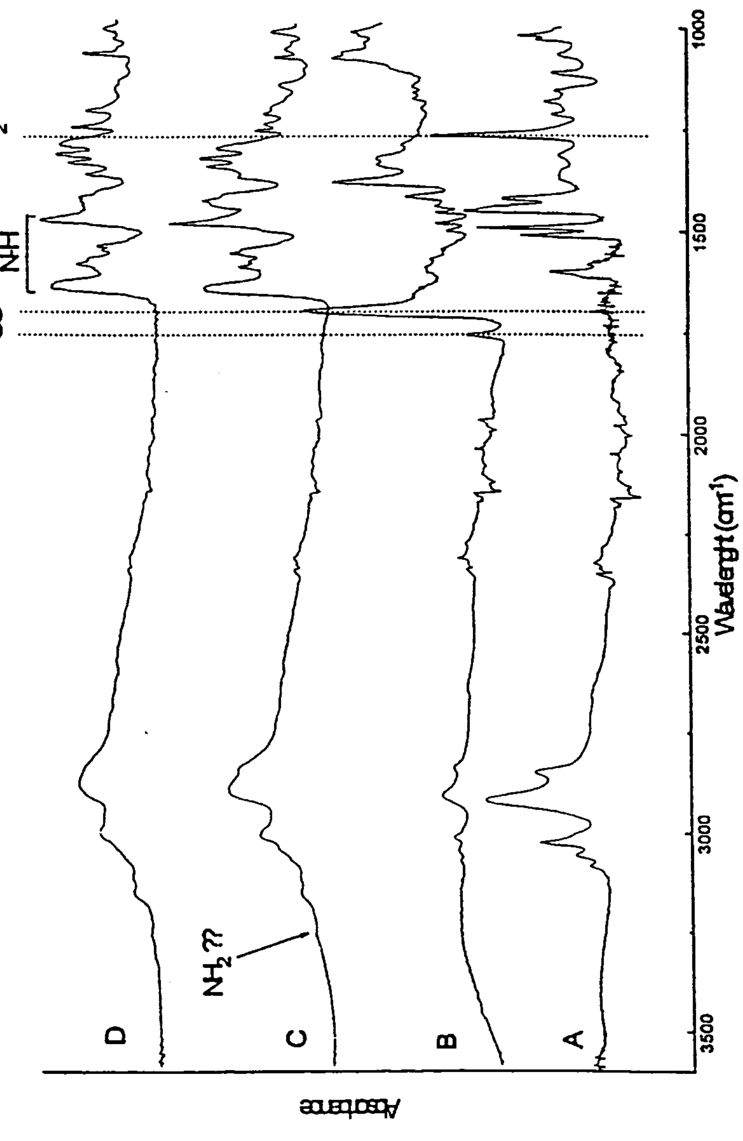
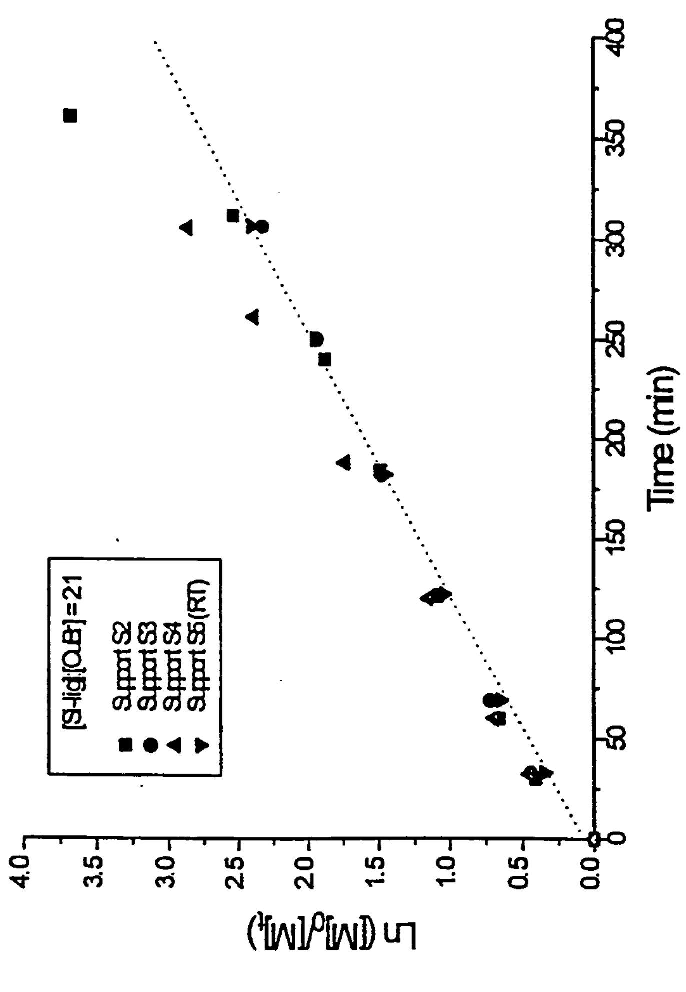

D
C
B
A
NH2 ??
CO
C=N
N-H
CH2Cl
Absorbance
3500
3000
2500
2000
1500
1000
Wavelength (cm-1)

Figure 3


Support S2
Support S3
Support S4
Support S5(RT)
Ln ([M]0/[M]t)
Time (min)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
0
50
100
150
200
250
300
350
400

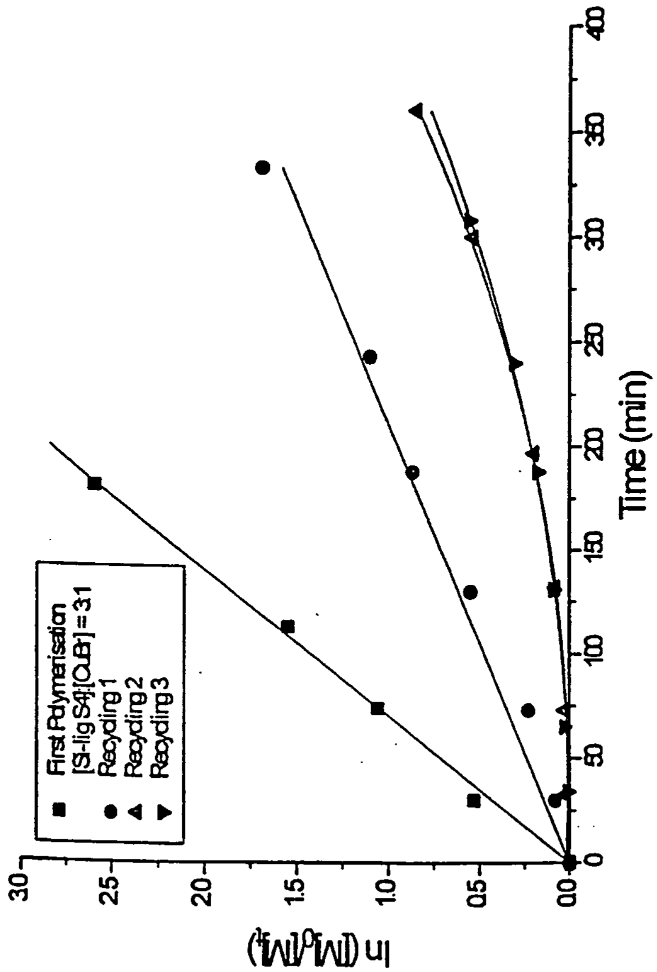

First Polymerisation
[S1-lig S4]:[CuBr] = 31
Recycling 1
Recycling 2
Recycling 3
Time (min)
ln ([M]$_0$/[M]$_t$)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0
50
100
150
200
250
300
350
400

Figure 4

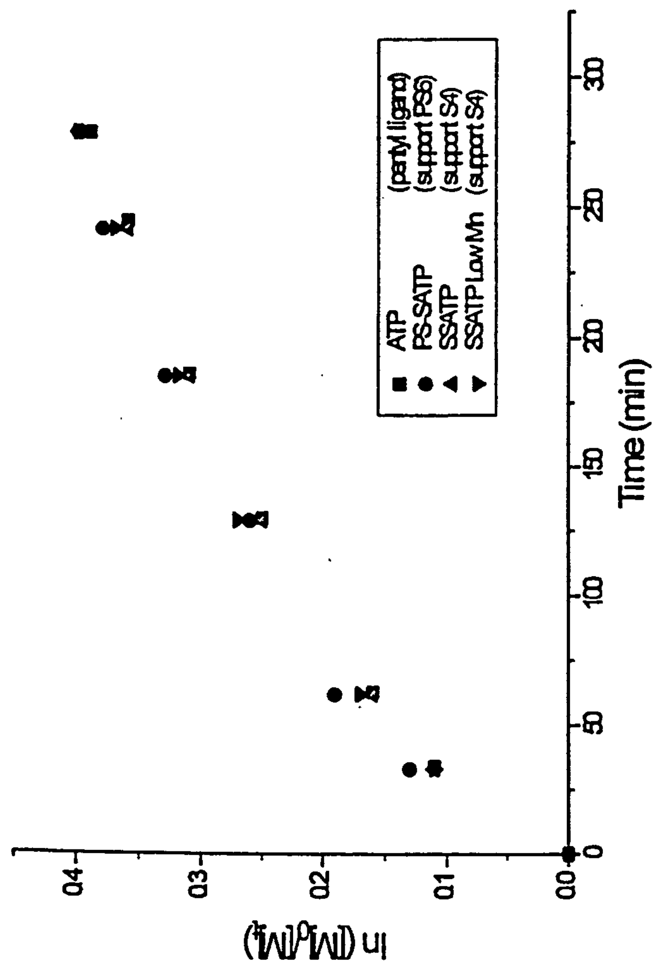

ln ([M]0/[M]t)
0.0
0.1
0.2
0.3
0.4
0
50
100
150
200
250
300
Time (min)
ATP (pentyl ligand)
PS-SATP (support PS5)
SSATP (support S4)
SSATP LowMn (support S4)

Figure 5

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 98/03592

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F4/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 558 143 A (ENICHEM SPA) 1 September 1993 see page 3, line 4 - page 5, line 58 see example 1	1,2,4-7, 16-18,28
X	see page 6, line 11 - line 16	29
X	see example 3	30
X	WANG Y ET AL: "Synthesis and selective catalytic oxidation properties of polymer -bound melamine copper(II) complex" REACTIVE & FUNCTIONAL POLYMERS, vol. 33, no. 1, May 1997, page 81-85 XP004082718 see page 81, column 1 see page 84, paragraph 3.5 see page 82, paragraph 2.2 see figure 1	1,2,4-7, 16,17

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
11 March 1999	01/04/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Fischer, B

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 98/03592

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	UOZUMI Y ET AL: "New Amphiphilic Palladium-Phosphine Complexes Bound to Solid Supports: Preparation and Use for Catalytic Allylic Substitution in Aqueous Media" TETRAHEDRON LETTERS, vol. 38, no. 20, 19 May 1997, page 3557-3560 XP004061958 see page 3557, paragraph 1 - page 3558, paragraph 1 see page 3558, paragraph 2 see figure 1 ---	1,2,4-7, 16,17
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P,Y	see page 54 - page 58	20-24, 29,32
	see example 1 see example 2 see example 5	
X	see example 3	25,26
X	see example 4 ---	28,30
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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PCT/GB 98/03592

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